# ELECTROPHORETIC STUDIES OF TURBIDITY REMOVAL BY COAGULATION WITH FERRIC SULFATE

By

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# I. INTRODUCTION

Clays are the most common source of turbidity in surface waters used for municipal and industrial water supplies. Before surface water is satisfactory for domestic and industrial use, most of the clay and other particulate matter present in the water must be removed. Removal of the suspended matter is usually accomplished by alum or ferric sulfate coagulation, sedimentation, and rapid sand filtration. Water treatment plants which utilize this process produce finished waters which regularly exceed the minimum quality required for potable water by the U. S. Public Health Service.[1,2,3] The specific Public Health Service recommendation concerning turbidity is that the turbidity of drinking water be less than five units.

Prediction of the optimum coagulation conditions for the production of such high quality water from a given raw water is very difficult. In the absence of records of previous treatment of water from the same source it is rationally impossible at present. The difficulty of coagulation prognosis is the result of complexly related effects of the numerous properties of the raw water and the chosen coagulation conditions which affect the efficacy of coagulation. Among these conditions and properties are: specific coagulant chosen, coagulant dosage, pH, alkalinity, ionic constituents, and base exchange capacity of the raw water; and size, shape, chemical nature, hydration, and charge of the colloidal particles in suspension. Most of the factors which affect coagulation also affect the electrophoretic mobility of the suspended

colloidal particles.

Electrophoresis is the movement of electrically charged particles, suspended in a conducting liquid medium, which results from the impression of an electric field. Electrophoretic mobility is the ratio of the speed of electrophoretic movement to the intensity of the electrical field which produced the motion. It is commonly expressed in microns per second per volt per centimeter.

Mineral content, coagulant, coagulant dose, alkalinity and nature of clay particles, of the numerous parameters which affect electrophoretic mobility and coagulation, can be chosen and controlled for a selected synthetic clay suspension. In addition to these parameters which can be selected, pH, base exchange capacity, effectiveness of coagulation and particulate electrophoretic mobility for a given suspension can be directly measured.

The present research has been performed in order to study the empirical relationships among electrophoretic mobility, residual turbidity, coagulant dosage, and residual iron (the measurable parameter) for the ferric sulfate coagulation of suspensions of three different clays over the pH range between three and ten. To my knowledge, such a study has not been attempted before. The relationships discovered are described herein, and the effectiveness of ferric sulfate coagulation of these clays is compared with that of their alum coagulation, reported earlier by Black and Hannah.[4]

## II. HISTORICAL REVIEW

The earliest records of the coagulation proce[illegible] by Blank[5] who wrote:

> Although various crude methods of water purification, generally characterized as coagulation, have been known and used since ancient times, knowledge of the fundamental factors involved in the process has been acquired comparatively recently.

The earliest references of scientific interest in coagulation as a process for the treatment of water are references to the works of D'Arcet[6,7] and Jeunet.[6,8] D'Arcet at the beginning of the nineteenth century and Jeunet in 1855 sought to establish the value of the process, but it was not used for the treatment of a public water supply until 1881. After its initiation in Bolton, England,[6] the process was soon adopted in Holland and in the United States.

The first coagulation patent was granted, in 1884, to Isaiah Smith Hyatt.[5] Following the suggestion of Col. L. N. Gardner, Superintendent of the New Orleans Water Company, Hyatt successfully treated turbid water by combining the use of perchloride of iron as a coagulant with his process of rapid filtration. His patent covered not only the use of perchloride of iron, but also of "any other suitable agent which is capable of coagulating the impurities of the liquid and preventing their passage through the filter bed."

The 1884 Annual Report of the State Geologist of New Jersey contained results of tests of various salts as coagulants. Austen and Wilber[6,9] concluded that of the salts investigated, aluminum sulfate was most effective. Fuller[10] published a description of similar studies

in 1898. He found sulfates of iron and aluminum to be most effective. The chlorides of these elements followed next in order, but their use as coagulants in water treatment has not developed on a practical scale.

In the year of Fuller's publication, W. E. Ball,[5] at Quincy, Illinois, began using a mixture of ferrous sulfate and lime for coagulation. Fourteen years later, E. V. Ball[14] reported the first use of chlorinated copperas. This chemical was not tried again until 1928, when Hedgepeth and Olsen[12] used it for the successful treatment of a highly colored water. Ferric ion was produced by oxidation of the ferrous sulfate with chlorine.

As use of the process has become prevalent, the number of researchers and the scientific disciplines they represent have proliferated. Black[13] and Packham[6] in recent reviews of coagulation theory and related literature, thoroughly cover the many facets of historical and contemporary research, theory, and practice. The literature cited in the present study will consequently be limited to that directly related to the research herein reported.

In 1923 the first of a series of studies by Theriault, Clark, and Miller was reported. The paper by Theriault and Clark[14] described their treatment of several buffered solutions with various amounts of alum to determine the effect of pH upon the rate of floc formation. They assumed that the optimum pH for coagulative treatment of water would be the pH at which the minimum time was required for the formation of the aluminum floc. They found that generally the best floc formation occurred in the pH range 4.95 to 5.40. Higher alum doses resulted in broader ranges of pH over which rapid coagulation was observed. These workers were unable to explain the differences between values of pH

which accompanied rapid coagulation in their study and the higher values observed to be most effective in water treatment plants.

In the same year, Baylis,[15] using alum to coagulate natural waters of varying alkalinity, noted that for a given pH, waters of higher alkalinity required larger quantities of coagulant to accomplish satisfactory treatment. For any chosen water he was able to reduce the alum dosage by adjusting the pH with a strong acid, thereby neutralizing a portion of the alkalinity originally present. The values of pH for optimum coagulation were in the range 5.5 to 7.0.

Late in 1923, Miller[16] published the second of the Theriault, Clark, and Miller papers. He described their constituent study of precipitates formed by the mixing of potassium alum solutions with sodium hydroxide solutions of various molarities. Although the anion concentration of the coagulant had no practical effect, the amount of alkali mixed with a given quantity of aluminum exerted considerable influence upon the composition of the precipitate. The ratio of aluminum to sulfate ion was determined for the floc over the useful pH range, but the exact chemical nature of the floc was not determined. His review of treatment plant records revealed that optimum coagulation occurred within the pH range 5.4 to 6.5.

In another series of tests (1925) Miller[17] investigated the effects of various anions upon the formation of floc in solutions of potassium alum. Generally, the anions of higher valence exerted greater influence upon coagulation, and less alkali was necessary in their presence.

The composition of precipitates from ferrous and ferric salt solutions was the subject of another 1925 publication by Miller.[18]

There precipitates from the iron salts were found to be very similar to floc from the analogous aluminum salts, except that they were formed at pH values significantly lower than the minimum pH values observed for alum floc and that they remain insoluble above the maximum pH at which alum floc exists.

The results of Miller's experimental work allowed him to make three statements concerning the optimum conditions for floc formation with both iron and aluminum coagulants. (1) There must be present in the water a certain minimum quantity of the metallic coagulant ion. (2) There must be present an anion of strong coagulating power such as the sulfate ion. (3) The pH must be properly adjusted.

In 1926 Bartow and Peterson[19] examined the effects of various salts upon the formation rate for alum floc over the useful pH range. Many of the salts studied increased slightly the rate of floc formation and extended, on the acid side, the pH range over which floc occurred.

In a paper published in 1926 and now regarded as a classic in its field, Matteson[20] described the coagulation of clay suspensions and the electrophoretic mobility measurement of clay particles as mobility was altered by various dosages of aluminum salts. His work demonstrated the effect of the different anions and cations upon particle charge. He specifically predicted the utility of electrophoretic studies in water coagulation investigations and pointed out the predominant role played by the hydrated oxides formed during coagulation.

In three articles Black and others[21,22,23] report investigations, made on a laboratory and semi-plant scale, of the effects of several anions upon the rate of floc formation for both aluminum and ferric salts. They proposed improved conditions for laboratory study of

coagulation. Also they recommended the use of larger samples and containers, constant stirring, and isohydric indicators. With such improvements they could duplicate pilot plant results. Anions were found to be useful to increase the rate of coagulation and to broaden the pH ranges of rapid floc formation. The pH range for floc formation was wider for ferric sulfate than for alum, but no iron floc formed between pH values 6.5 and 8.5. The authors stressed the importance of adsorption as an important mechanism of turbidity removal and also attributed zones of no floc formation to a change in particle charge.

In the slightly more than a decade since the publication of Black's 1934 article, the interest of water chemists seem to have been focused upon activated silica and other coagulant aids. The work of Langelier and Ludwig[24,25] marked the return of many researchers to the field of basic coagulation theory. They initiated the use of synthetic clay suspensions and called attention to the importance of base exchange capacity and particle size distribution of raw water, the action of metallic hydrolysis products as "binders," and the occurrence of perikinetic coagulation.

In 1950, Filipovich, Black, and others[26] examined the relationships among pH, zeta potential, base exchange capacity, coagulant dosage, and turbidity removal for the coagulation of suspensions of five clays with alum. Clays of high base exchange capacity required considerably larger doses of coagulant to accomplish coagulation than did clays of lower base exchange capacity. The authors reaffirmed the superior effectiveness of hydrolysis products over that of trivalent aluminum ions as coagulating agents.

Matijevic and others[27] (1961) coagulated lyophobic colloidal

suspensions of known particle charge and concentration with aluminum nitrate to determine the nature of the species formed during alum floc formation. Results indicated that below pH 4 the simple trivalent hydrated aluminum ion prevails. Between pH 4 and pH 7 the probable prevailing complex is the tetravalent $Al_8(OH)_{20}^{4+}$. At higher pH values the tetravalent hydrate is transformed into a divalent form which in turn yields to a complex of zero charge.

In the same year Black and Hannah,[4] using alum and various polyelectrolyte coagulants and coagulant aids, investigated the relationships among pH, electrophoretic mobility, base exchange capacity, coagulant dosage, and turbidity removal for the coagulation of three different clay suspensions. Several equivalents of coagulant per equivalent of clay base exchange capacity were necessary to effect satisfactory coagulation. The pH range of best coagulation was 7.5 to 8.5 in which range the electrophoretic mobilities of the clay particles was slightly negative. In some cases fair particikinetic coagulation occurred at pH values less than 4.5.

In his study of the precipitation of aluminum hydroxide resulting from addition of alum to solutions containing bicarbonate, carbonate, or chloride of sodium, Packham[28] (1960) evaluated the degree of precipitation by measuring soluble aluminum residuals and by photometrically recording turbidity of the system as a function of time. The maximum amount of precipitate was formed in the pH range 5.5 to 7.2. Maximum coagulation rate occurred between pH 7.2 and 7.6, and maximum immediate precipitation was observed at pH 7.1 or 7.2.

As his criterion of coagulation effectiveness, Packham chose the coagulant dosage required to reduce the initial turbidity by one-half

for a given set of conditions. The pH range he observed for optimum coagulation conditions based upon the use of this criterion does not agree with the pH range for good coagulation which others have reported. The difference results from the selection of different coagulation efficiency criteria. Use of Packham's criterion to select conditions for coagulation in a treatment plant would result in water of unsatisfactory quality. If he had chosen a much greater turbidity removal efficiency as his criterion, his prediction of optimum coagulation pH range would have coincided with those commonly reported.

Packham expressed the opinion that the coagulation of clay is principally accomplished by the encasement of the clay particles in the metallic hydroxide precipitate formed by reaction of the coagulants. Orthokinetic coagulation is the term now used to name the mechanism he described.

Hackrle[29] (1962) has presented arguments favoring the acceptance of the physical theory of stability and coagulation of colloidal clay suspensions. He has attached greater significance to the value of the zeta potential, the potential difference between the "Helmholtz layer" and the bulk of the suspending medium, than to the value of the zeta potential, the potential difference between the plane of shear and the bulk of the suspending medium. He has suggested that the metallic coagulants react to form crystalline hydrous oxide sols which destabilize the clay suspension by mutual coagulation. His conclusions were based upon his work with ferric sulfate and clay suspensions and upon crystallographic studies of such precipitates reported by others. In his tests pH and coagulant dose were allowed to vary simultaneously, and no measurements of electrophoretic mobility were performed to

permit an examination of the independent relationships among pH, coagulant dosage, turbidity removal and zeta potential.

In 1962 Stumm and Morgan[30] cited the work of others and identified, for both iron and aluminum salts, the hydrolysis products of highest effective charge and assigned tentative formulae to them. They also called attention to the aging effect of iron and aluminum sols and emphasized the chemical nature of particle charge caused by ionization as contrasted with charge produced by physical adsorption. The majority of their laboratory tests were performed to determine the specific chemical interaction between various functional groups normally found in water and the metallic coagulants in common use. They concluded that metallic complexes other than hydrous oxides can be formed as a result of the interactions and that the interaction of the functional groups can appreciably affect the pH at which optimum conditions of coagulation occur. They also presented a method for carrying out laboratory jar tests at constant pH and convincingly justified the desirability of such a procedure.

## III. COAGULATION THEORY

Any explanation of coagulation theory must be preceded by a description of the physical and chemical characteristics of the colloidal suspensions to be coagulated. The suspensions customarily encountered in the treatment of water for municipal and industrial use are dilute. Even where raw water is taken from streams which carry heavy sediment loads, the water to be coagulated is dilute because presedimentation is used to remove the readily settleable particles. The materials which are removed from the dilute suspensions by coagulation can be generally classified as turbidity or "color."

In their study of the nature of colored surface waters Black and Christman[31] have ascertained that "the materials responsible for color in water exist primarily in colloidal suspension in the water." They found particle size and number of particles to vary with pH, but particle size was generally less than 10 mu. Although the present research is not directly concerned with coagulation for color removal, color compounds do merit mention, because their colloidal nature and susceptibility to coagulation are similar to those of colloidal turbidity particles.

The primary source of turbidity to which the present investigation pertains is colloidal clay. Clays are complex aluminum silicates of sedimentary origin. Their lattice structures consist of layers of silicon-oxygen sheets and aluminum-oxygen sheets. These sheets, common to all clays, occur in different orders in the different classes of clays.

Kaolinite, montmorillonite, and fuller's earth have been used in the present research.

An important physico-chemical characteristic of clays which is considerably affected by the placement order of the sheets is base exchange capacity. Kaolinite and montmorillonite, of the clays used in the present research, represent the low and high extremes of base exchange capacity which results from crystalline structure.

Kaolinite consists of an alumina sheet and a silica sheet which are combined to form one layer, whereas montmorillonite has an alumina sheet included between two silica sheets to form one layer. These layers have a definite thickness, measurable by x-ray diffraction methods, which is constant for a specific clay, but the lattices extend to the irregularly broken edges of the crystals in the other two directions. In water the parallel layers tend to split apart and become dispersed. Because of the small coulombic forces between similar adjacent silica sheets in montmorillonite, the surfaces of the layers become hydrated and therefore separate to a considerable extent. Kaolinite layers are held together tightly by hydrogen bonding between hydroxide ions on the bottom of one layer and oxygen ions on top of the next layer and thus resist separation. A more detailed discussion of clay structure is given by Kerr.[32]

Marshall and Krinbill[33] have stated one of the results of the structural differences between kaolinite and montmorillonite. The base exchange capacity of kaolinite varies with particle size, whereas the base exchange capacity of montmorillonite is almost independent of particle size.

Particle size is the property upon which the definition of

colloids is based, but colloid behavior results from phenomena involving the tremendous surface area inherent in particles of colloidal size. An example of the importance of surface phenomena is that the classifications of colloids, lyophilic and lyophobic, result from such a phenomenon. Distinction between the two classes depends upon the wettability of the surface of the particle. The particles possessing poorly wettable surfaces are called lyophobic. Lyophobic colloids are unstable, because by coalescing they offer a smaller surface area at which a solid-to-liquid interface must be formed. Since the smaller interface results in a lower surface energy state and a lower total energy state for the system, the coalescence is spontaneous.

Lyophilic colloids, on the other hand, are stable because of the attraction of the surface for the solvent -- the wettability of the surface. These lyophilic colloidal solids which exhibit surface interaction with the solvent are, therefore, the colloids of primary concern to water chemists.

Another surface phenomenon which greatly influences the properties of a suspensoid is the electrical charge possessed by the particles. The charge can be initiated by several different surface mechanisms; still other surface phenomena effect charge magnitude and sign.

Of the several mechanisms which can produce particle charge, we shall first consider the process that might be termed preferential ionization. As an example of this mechanism, we shall consider minute crystals of silver iodide in equilibrium with a saturated solution in which the ionic concentration product is roughly $10^{-16}$. The forces with which the two ions are held in the lattice differ greatly. Despite its larger size, the more polarizable iodide ion is held much more

forcefully than is the silver ion. When the concentrations of the two ions in the solution are equal, more silver ions escape into the solution than do iodide ions; hence, the crystals are negatively charged. If the silver ion concentration is increased, the charge can be reduced to zero, a further increase of silver ion concentration can cause a charge reversal.

Ionization of functional groups which are connected to the particle by covalent bonds is a second and important source of particle charge. Examples of particles thus charged are proteins and ion exchange materials. Proteins are formed by long chains of amino acids joined by peptide linkages. Some of these amino acids carry an additional carboxyl or amino group which can remain free and exposed to the solvent. Thus they can form $COO^-$ and $NH_3^+$ ions which are covalently attached to the particle. The ion exchange materials are porous solids which have built-in acids or basic groups. The natural zeolites and many clays are included in this general category.

Among the other mechanisms which can cause particle charge are chemisorption and adsorption of specific ions resulting from van der Waal's forces. For particles which are charged by the adsorption of specific ions, the surface charge density is greatly affected by concentration changes of these ions in the solution.

In all of the mechanisms mentioned above, particle charge was achieved by the separation of unlike charges (the destruction of electroneutrality). Because of the large amount of energy involved in the separation of these charges, electroneutrality is disturbed only on the ultramicroscopic scale. When any one, or a combination of these mechanisms, produces an excess of charges of one sign in any locality,

there must exist an equal excess of charges of opposite sign in the immediate vicinity. Thus, we find surrounding and very near each charged particle an excess concentration of ions of counter sign. These ions are called counterions or gegenions. The counterion excess occurs only in the solution very closely surrounding each charged particle. Throughout the rest of the suspending medium electroneutrality prevails.

When we speak of electroneutrality and areas of excess charge, we implicitly assume that the conditions we describe are the averages, with respect to time and space, of the several dynamic equilibria which prevail. Brownian movement is one spatial equilibrium which must be averaged. Ion exchange is a physico-chemical equilibrium of considerable effect. Each of the equilibria, including these two, cause fluctuations with respect to time.

Based upon these averaged conditions, several models have been proposed to explain the possible arrangement of the charged surface and its surrounding array of counterions. These models have been used by chemists, physicists, and mathematicians as bases for their computation of theoretical values of parameters for many colloid systems. Probably none of the models proposed is correct, but each has been useful in the explanation of some observed phenomenon.

The simplest of these was proposed by Helmholtz.[34] Fig. 1 is a schematic section which shows the charged surface and the surrounding medium. By ionization or some other mechanism, the surface of the particle is charged. This excess of negative charge in or on the surface attracts toward the surface the positive ions in the solution. Helmholtz proposed a model in which all of the counterions so attracted

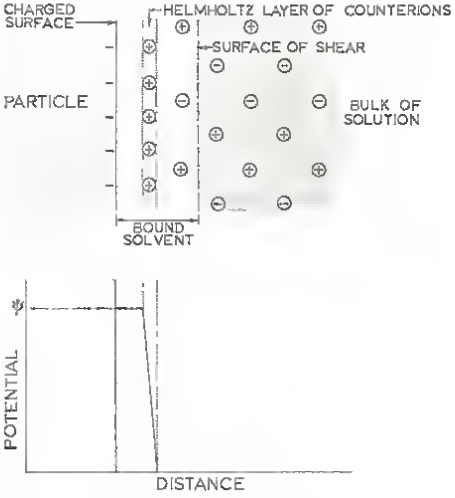


FIG. 1 -THE HELMHOLTZ LAYER MODEL

are located in a single surface parallel to and very near the surface of the particle. His model is analogous to a parallel plate condenser. The graph of potential in Fig. 1 represents the potential difference between the bulk of the solution and the point within the solid-liquid interface that corresponds with the abscissa.

Fig. 2 depicts the Gouy-Chapman[35] model which is named for the two scientists who first considered it in detail. They recognized the Helmholtz assumption to be an oversimplification of the spatial arrangement of the neutralizing counterions. Reasoning that thermal agitation would prevent such an uniform arrangement of gegenions, they proposed a diffuse layer of variable but finite thickness which contains an excess concentration of counterions. In formulating their model they also considered the shielding effect of the counterions located near the particle upon the attractive force existing between the particle and the more distant counterions. The proposed model is characterized by a potential versus distance graph, for which the potential decreases at a decreasing rate as distance from the surface of the colloid increases.

In addition to the gegenions which are attracted to the particle, a sheath of the solvent is tightly bound to lyophilic colloids. This sheath is pulled along with the colloid whenever some force such as that of gravity causes relative motion between the particle and the bulk of the solvent. Thus, there exists surrounding a colloid a surface of shear which contains the bound solvent that accompanies the particle as it migrates.

If an electric field is impressed upon a colloid system, the colloids migrate toward the pole of opposite charge at a speed

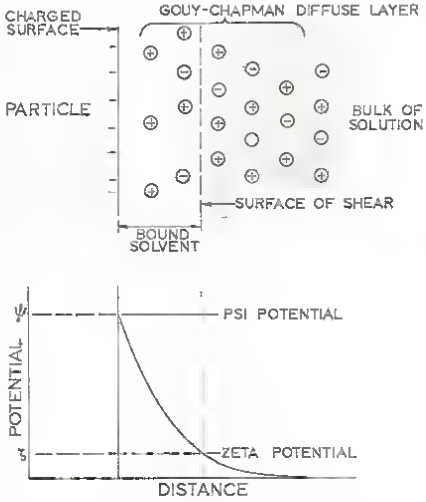


FIG. 2 -THE GOUY-CHAPMAN DIFFUSE LAYER MODEL

proportional to the potential which exists between the surface of shear and the bulk of the solvent. (The "bulk of the solvent" refers to the portion of the solvent out of the effective interaction range of the charged colloids, that is, where electroneutrality occurs on micro as well as macro scale.) This shear surface potential upon which the velocity of a charged colloid in an electric field depends is called the zeta potential, $\zeta$. The movement of the charged colloid that is caused by impression of the electric field is referred to as electrophoresis, and the ratio of particle speed to the intensity of the electric field is termed electrophoretic mobility. In units commonly used for expression of mobility and potential, a $1\mu/sec/v/cm$ mobility is equivalent to a potential of 13 mv.

Since the velocity of colloid movement caused by a measurable field intensity can be observed through an ultramicroscope or by moving-boundary frontal methods, the electrophoretic mobility of colloids is a directly measurable parameter. This parameter is closely related to particle charge, surface-charge-density diffuse-layer thickness, and particle surface potential, which are important parameters but are not directly measurable. (The surface potential, $\psi$, mentioned above is diagrammatically presented in Fig. 2).

A model suggested by Stern[36] represents further sophistication of the Gouy-Chapman diffuse layer theory. It includes the Stern layer of adsorbed counterions which are held in actual contact with the surface of the colloid. A section of the Stern model and a typical potential curve for it appear in Fig. 3. In addition to the zeta potential and the surface potential, $\psi$, the potential at the interface between the Stern layer and the Gouy-Chapman portion of the double diffuse

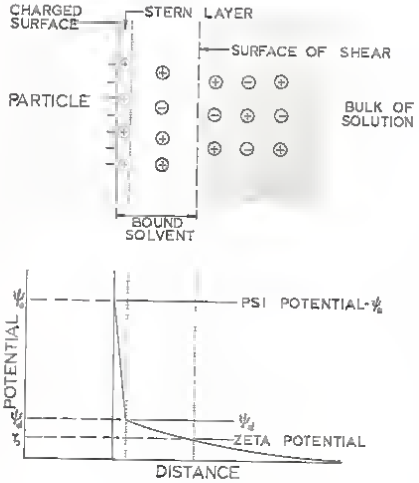


FIG. 3 -THE STERN LAYER MODEL

layer is indicated and represented by the symbol $\psi_d$.

The models described above are useful as they provide a basis for appreciating the phenomena which influence the stability or instability of a given colloidal suspension. The primary phenomenon favoring stability is, of course, the mutually repulsive force between similarly charged colloids.

A particle with its complete double layer is electrically neutral, so that it exerts no net coulombic force upon another. This situation exists in the case of particles which are sufficiently distant from each other. As two particles approach, however, the double layers interpenetrate and interact. Should the two particle surfaces finally touch, there would be no more diffuse layers between them to screen them from the effect of the repulsive coulombic force. It is the work required to thus distort and finally destroy a part of the diffuse double layers which causes most of the repulsion.

Charge density upon the particle surface and concentration of ions in the solution surrounding a particle are parameters which directly affect stability. Low ionic concentration in the solution causes greater thickness of the diffuse layer. High charge density results in large psi potential. Thus low ionic concentration and high charge density contribute to colloid stability. The relationship of these parameters to zeta potential can be seen in Fig. 1. The conditions which contribute to stability result in high values of zeta potential; therefore, zeta potential, or more important, the directly measurable electrophoretic mobility can be a useful index of stability. A less important phenomenon contributory to stability is the van der Waal adsorption of simulations. This occurs to a significant degree

only under very specialized conditions, and the effect is more important with emulsions of large molecular weight.

The phenomena which are influential toward instability are much more numerous than those causing stability, because the former consist of all the phenomena which can impair the effectiveness of the latter. Of the instability mechanisms, the two most important are the mutual attraction (and coagulation) of oppositely charged colloids and the van der Waal attraction. The other mechanisms are of much less direct importance, or they effect instability through their influence upon or in conjunction with one of the two mechanisms mentioned.

Van der Waal forces are always attractive; but because they result from dipole interaction, they decrease approximately with the third power of the distance between the particles. Thus they are effective only when the particles are brought into extreme proximity. Coulombic forces between similarly charged colloids oppose their approach toward each other with force which decreases roughly with the second power of the distance between the particles, so that some other force is required to push them close enough together for van der Waal forces to prevail. Brownian motion caused by thermal agitation is one source of such force. Mechanical agitation of a suspension can similarly contribute to instability.

Some other factors effect instability by reducing the particle charge or potential of the colloids. The concentration of "potential determining ions" in the solution exerts a large influence upon this parameter. The hydrogen ion concentration will determine the charge density and, hence, the potential of any particle which depends upon the ionization of carboxyl or amine groups as its source of charge.

The concentration of inert ions in the solvent can affect stability by increasing the probability of particle collisions as their number is increased and by causing compaction of the diffuse layer.

Ionic concentration is not the only ionic variable which influences stability. The valence and size of the specific ions present exert effects upon particle charge and potential. The Schulze-Hardy rule is a general statement of the observed phenomena that divalent counterions are more potent in the production of instability than monovalent counterions and that trivalent ions are much more powerful coagulation agents than the divalent counterions are. Ion size and less important anomalous characteristics of specific ions influence their ability to cause colloid instability as is evidenced by the Hoffmeister series in which various anions and cations have been listed in order of flocculating power.

Because of the numerous mechanisms which are responsible for destabilization, the many variables which affect stability, and the differing chemical and physical nature of the sundry colloidal particles which may be encountered, it is practically impossible to calculate the conditions under which satisfactory coagulation of a given colloidal suspension will occur. It is desirable, therefore, to examine the empirical relationships of the parameters that can be measured so that the work involved in cut-and-try coagulation can be reduced.

## IV. PURPOSE AND SCOPE

The preceding chapters have reviewed the most significant work dealing with water coagulation and have summarized contemporary theories concerning the basic mechanisms involved. Because of the complexity of relationships among the numberous variables which affect coagulation, many researchers have sought to discover empirical relationships among the measurable parameters in order that they might more fully understand basic coagulation mechanisms.

Black and Hannah,[4] Filipovich and others,[26] Black and Willems,[37] and Black and Christman[38] have pursued such courses in the electrophoretic studies of the coagulation of several colloidal materials with various coagulants and coagulant aids. Packham[39] and Haskins[29] have reported some ferric sulfate coagulation research, but neither of them performed electrophoretic studies of coagulation in which the effects of coagulant dosage and pH have been separately determined.

The primary purpose of the present research is to add to the body of knowledge resulting from the work of Black, Hannah, Willems, Christman, and Filipovich. It will seek to learn the relationships among electrophoretic mobility, residual turbidity, coagulant dosage, and residual iron content of three clay suspensions resulting from their ferric sulfate coagulation. The three clays were chosen so that suspensions containing equal concentrations of them would exhibit low, medium, and high base exchange capacities respectively. The literature contains no references to work of this nature.

Because certain materials and procedures were utilized, the study, in addition to its primary purpose, will allow direct comparison of the results of ferric sulfate coagulation with the results of alum coagulation of these clays reported by Black and Hannah.[4] Moreover, the results of these tests may yield experimental confirmation of coagulation theories previously presented by others.

The scope of the work was limited to study of electrophoretic mobility, residual turbidity, and residual iron content in the ferric sulfate coagulation of suspensions of a low, a medium, and a high base exchange capacity clay over the pH range 3 to 10. The ferric sulfate dosages were 0, 3, 5, and 50 mg/l respectively. The procedures involved were jar tests, residual turbidity and iron determinations, and electrophoretic mobility determinations.

## V. EXPERIMENTAL MATERIALS AND PROCEDURES

The experimental portion of the research consisted of (1) jar tests for the ferric sulfate coagulation of three clay suspensions and (2) the determination of mobilities for the flocculating colloids in these suspensions. Coagulant dosages of 0.0, 3.0, 5.0, and 50 mg/l of ferric sulfate were used, and pH was varied over the range 3 to 10. Final dissolved iron content, final pH, and initial and final turbidity of the jar test suspensions were measured, and pH values of mobility samples were determined.

### Materials

Clays

The clays used to prepare turbid waters were Kaolinite 4 and Montmorillonite 23, obtained from Ward's Natural Science Establishment, and fuller's earth, obtained from the Floridin Company.

Ferric Sulfate

The ferric sulfate used as coagulant was the commercial grade manufactured by the Tennessee Corporation, Atlanta, Georgia. Ferri-Floc is the registered trademark by which the manufacturer designates this material. The analysis of the particular sample of ferric sulfate used appears in Table 1.

TABLE 1

ANALYSIS OF FERRIC SULFATE USED FOR COAGULATION

| Constituent | Per Cent by Weight |
|---|---|
| Total Water Soluble Iron | 21.50 |
| Water Soluble Ferrous Iron ($Fe^{++}$) | 0.70 |
| Water Soluble Ferric Iron ($Fe^{+++}$) | 20.80 |
| Water Insoluble Matter | 2.00 |
| Free Acid (as $H_2SO_4$) | 2.55 |
| Moisture | 2.51 |

## Procedures

### Preparation of Clay Suspensions

Harman[40] has given the following description of the clays used and of the first steps in their preparation:

> The kaolinite and montmorillonite consisted of large lumps of dry clay. These materials were crushed and ground with mortar and pestle and were then ball-milled for 24 hours. The fuller's earth, which was obtained as a dry powder, was ball-milled for 24 hours.

The preparatory efforts of others, described above, were performed early in 1939. At that time Harman[40] determined the base exchange capacity of each of the three clays in the manner prescribed in Official Methods of Analysis of the Association of Official Agricultural Chemists.[41] Since their preliminary preparation the dried clays had been stored in closed glass containers. With the clays in the condition described, the present experiment was begun with the weighing out of four 3.75-g aliquants of each clay. Each aliquant, in turn, was mixed with 500 ml of demineralized water and dispersed by mixing in a Waring Blendor* for five minutes. The four aliquants of each clay suspension were placed in a separate covered beaker and allowed to hydrate for 24 hours. At the end of the hydration period, each suspension was slowly passed through a sodium-cycle, ion-exchange column to replace the natural, exchangeable cations of the clay with sodium ions. A glass column of 25 mm diameter containing a 12-inch depth of Nalcite HCR cation-exchange resin was used for the ion exchange process, which was

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*The Waring Blendor is manufactured by Waring Products Company, New York, New York.

[illegible] Just before the treatment of the three clay suspensions the resin in each was regenerated with one liter of ten per cent NaCl solution.

Stock suspensions were prepared by diluting each of the three suspensions to twenty liters with demineralized water. The three suspensions were stored in polyethylene carboys.

Preparation of Ferric Sulfate

A 2-kg portion of commercial-grade ferric sulfate was taken from a 100-lb bag of the material which was supplied by the manufacturer. After being mixed thoroughly, the sample was quartered, and 500 g were reserved for analysis. Approximately 100 g of the remaining material was finely ground with mortar and pestle. Aliquants of 1 000 g were weighed out and stored in glass vials having tight-fitting polyethylene stoppers.

Because the hydrolysis reactions of ferric sulfate are dependent upon time and concentration, a fresh coagulant solution of the chosen concentration was prepared daily. One of the previously weighed aliquants was quantitatively transferred to a 200-ml volumetric flask, which was then filled to the mark with demineralized water. This particular concentration was chosen, because less concentrated solutions became cloudy and were found to contain considerable volumes of hydrolyzed material within four hours after the initial mixing. A minimum of twenty minutes was allowed for the mixing, which was accomplished with a magnetic stirrer.

Coagulation Tests

Sample preparation. After the preparation of the aforementioned clay suspensions, approximately six months passed before coagulation tests were begun. A high-speed mixer, equipped with a stainless steel shaft and propeller, was used to thoroughly mix the suspensions. The minimum time of mixing for any suspension was one hour. Mixing was continued while 200-ml aliquants were pipetted into 8-oz polyethylene bottles. Also, triplicate 25-ml samples of each suspension were pipetted into beakers, and residue upon evaporation was determined for each in accord with the procedure specified in Standard Methods for the Examination of Water and Wastewater,[43] which hereafter will be referred to as Standard Methods. To provide an ionic concentration in the suspensions comparable to those of surface waters, 20 ml of 5.00-g/l sodium bicarbonate solution was added to each of the 200-ml suspension aliquants. In the final clay suspension samples, diluted as described below, the sodium bicarbonate concentration was 50 mg/l.

In the morning of a typical day of coagulation tests, immediately after preparation of the coagulant solution, six of the 8-oz bottles containing the desired clay were selected, and their contents were quantitatively transferred to separate two-liter volumetric flasks in which 500 ml of demineralized water had been placed. Ten ml of chlorine solution containing 0.400 g/l of $Cl_2$ were pipetted into each flask. (During chlorine demand tests, that specific quantity had proved sufficient to satisfy the demand of the suspensions and still to leave about 1 mg/l of free available chlorine to oxidize the ferrous iron present to

the ferric state. Such a prechlorination dosage is common for treatment of surface water.) Sufficient amounts of 0.1 N NaOH or HCl were added to the flasks to yield the desired pH of the final suspension, and the flasks were filled to the mark with demineralized water. A teflon-covered magnetic bar was placed in each flask, and the flask's contents were mixed for five minutes with a magnetic stirrer. One-liter graduated cylinders were used to transfer half of each flask's contents to separate 48-cm square jars which were placed on the multiple laboratory stirrer* (hereafter referred to as the jar test machine). The remaining contents of the flasks were retained for mobility determinations.

Flocculation. The flocculation process was begun by rapidly stirring the suspensions while adding the correct coagulant dosage to each of the six suspensions. After receiving the coagulant dosages, the suspensions were mixed rapidly for 2 minutes and then slowly for 28 minutes. Next the stirring paddles were removed, and the suspensions were allowed to settle for 10 minutes. The rate chosen for rapid mixing was 100 rpm. The speed initially selected for slow mixing was 40 rpm, but soon after laboratory tests were begun, 5 rpm was adopted for slow mixing since it appeared that higher rates might cause disintegration of the flocculles.

Promptly at the end of the sedimentation period 250-ml samples were drawn from each jar. An apparatus similar to that described by Cohen[44] was used to siphon each sample from approximately an inch below the surface of the supernant. The settled samples so obtained were used for residual turbidity and residual iron determinations.

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*The six-jar, variable-speed stirrer used is a product of Phipps and Bird, Inc., Richmond, Virginia.

Initial and residual turbidity measurements. Turbidity of [illegible] samples was measured in a Lumetron Model 450 Filter Photometer.* The procedure recommended by the manufacturer[45] required the preparation of a calibration curve for each of the three clays used. Calibration for a single clay involved the preparation of eight to ten suspensions so that their turbidities uniformly covered the desired turbidity range. The optical density of each suspension was measured in the Lumetron for 650-mμ light over a 75-mm path. Also, the turbidity of each of the suspensions was determined with the Jackson Candle Turbidimeter in the manner set forth in Standard Methods.[46]

Because coagulation efficiency was to be judged upon the basis of turbidity removal, determinations of initial turbidities was necessary. An average value of initial turbidity for each of the three clay suspensions was obtained by measuring the initial turbidity of the suspensions for the jar tests, in which coagulant dosage was zero.

Residual iron determination. The supernatant samples which were obtained in the manner described above were filtered prior to the determination of their iron content. A fine, smooth, quantitative filter paper† was used. Filtration was necessary, because some of the iron present was chemically or physically bound to floc particles of such small size that they did not settle out in the short settling period allowed. In a water treatment plant the iron bound to such small

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*The Lumetron Photometer is a product of Photovolt Corp., New York, New York.

†The paper used was paper No. 1306l manufactured by Will Corp., New York 52, New York.

flocculus would not be found in the finished water, because sedimentation of longer duration or passage through the rapid sand filter would remove them. Filtration of the iron samples thus makes the laboratory jar tests more nearly analogous to plant conditions. The iron content of unfiltered samples was determined without prior filtration. In a later chapter results of these determinations are identified and are compared with results for similar filtered samples. The variance of iron content between the two kinds of samples emphasizes the necessity for filtration.

The phenanthroline method appearing in Standard Methods[47] was followed for the iron determinations. A 530-mμ filter and a 75-mm light path were chosen for the Lumetron Model 450 Filter Photometer used for the colorimetric iron determinations.

Measurement of pH. The final pH of the coagulated clay suspensions was measured with a Beckman Model G pH meter.*

Electrophoretic Mobility Determinations

Dosing and mixing. A period of four to eight hours usually elapsed after the final dilution of the clay suspensions before mobility determinations were made. In order to attain thoroughly mixed suspensions after the quiescent period, each suspension was stirred for five minutes on a magnetic stirrer just prior to the mobility determinations. The individual suspensions were dosed with the appropriate amounts of coagulant at the beginning of the mixing.

*The Model G is a product of Beckman Instruments, Inc., Fullerton, California

Conductance measurement. Specific conductance was determined by the procedure described in Standard Methods.[48] A Model RC16B2 Conductivity Bridge* with a pipette-form conductivity cell having a cell constant of 1 $cm^{-1}$ was used for the measurements.

Measurement of pH. The pH of each suspension was measured immediately before the mobility of its particles was determined. A Beckman Model G pH Meter was used for these measurements.

Particle mobility measurement. The equipment and procedures used for the microelectrophoretic mobility determinations are those described in the paper by Hlask and Smith.[49] The detailed description of the physical dimensions and construction methods for the glass cell appear in an article by Briggs,[50] who designed it and for whom it is named. Since both procedure and equipment are described in detail in the references cited, only a general discussion of them will be included here. In addition to the general account, however, any deviation from the suggested methods of Hlask and Smith will be delineated specifically.

The Briggs cell is constructed of Pyrex† glass. Its rectangular cross-sectional shape and area are practically constant over the central portion of its longitudinal axis. A filling funnel is located at one end, and removable electrodes and outlet stopcocks are connected to either end of the cell. It is mounted in a metal stand which holds it in proper position on the microscope stage and supports it when it is not in use. Fig. 4 is Tombs's sketch[51] of a Briggs cell.

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*The Conductivity Bridge is a product of Industrial Instruments, Inc., Cedar Grove, New Jersey.

†Pyrex is a product of the Corning Glass Company, Midland, Michigan.

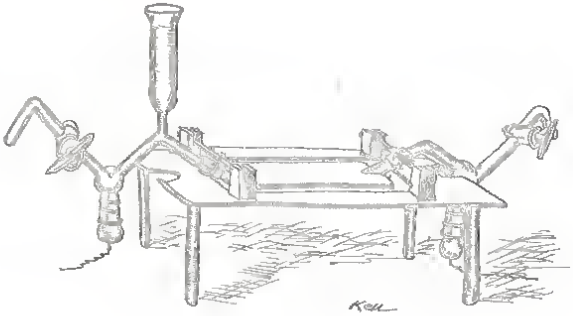

FIG 4 – THE BRIGGS CELL

Two Briggs cells were assembled, mounted, and calibrated before jar tests and mobility determinations were begun. Plastic Wood* was found to be a more satisfactory packing material than any previously tried. If removal from the holder is ever necessary, the cell can be freed easily by soaking the assembly in acetone or a similar solvent.

During the course of this study several improvements in technique were developed. (1) The cell holder was attached to the microscope stage with a pair of small clamps. This procedure prevented accidental misalignment of the cell during determinations. (2) Another deviation from the suggested procedure was the use of a 4-mm glass bead in each of the electrodes to prevent rapid mixing of the mercuric nitrate and potassium nitrate solutions in the electrode. This procedure was proposed by Briggs.[50] (3) It was found that the mercuric nitrate solution could be introduced into the electrode most easily with a hypodermic syringe fitted with a 2-in needle. (4) When sufficient mercuric nitrate solution was injected to bring the liquid level about 3 mm above the narrowest portion of the opening between the upper and lower chambers of the electrode, no trouble was experienced in placing the glass bead without entrapment of air bubbles beneath it.

Serendipitously it was discovered that for the suspensions studied, electrodes prepared in the manner described above could be used over periods as long as a week. Moreover, for these particular suspensions it was possible to rinse the cell by passing deionized water through it while it remained clamped in place on the microscope stage. The application of a low-intensity vacuum to the outlet tube caused

*Plastic Wood is a product of Boyle-Midway, Chamblee, Georgia.

water velocity of sufficient magnitude to remove the settled flocculeo; therefore, it was not necessary to remove the cell from the microscope stage more often than once a week. Once the system was aligned and the cell clamped securely in place, a check was necessary only at the beginning and ending of each day's determinations to be sure that the microscope was focused on the stationary layer inside the wall. The water aspirator which was used to pull cleaning water through the cell was also useful as an aid in filling the cell with a suspension without the entrapment of bubbles.

The particle velocities were determined by visual observation and were timed with a stopwatch. A previously calibrated ocular micrometer located in the plane of the microscope image of the stationary layer served as the measured course over which the flight of the particles were timed. The polarity of the electrodes was alternated between individual timings. Thus, of the twenty particles timed for each suspension, ten were observed to move toward the left, and ten moved toward the right. An exception to this characteristic movement was noted at the isoelectric point. At the isoelectric point various particles were observed simultaneously to move very slowly toward either electrode. The mobility of the particles of a suspension was computed from the mean of the time observed for each particle to travel a fixed distance; therefore, the computed mobilities are time-averaged rather than velocity-averaged mobilities.

[illegible] preparation of the suspensions studied have been described in preceding sections. Table 2 presents the turbidities, electrometric concentrations, and base exchange capacities of these suspensions.

TABLE 2

[illegible] OF THE CLAY SUSPENSIONS

| Clay | Initial Turbidity | Passing Upon Evaporation mg/l | Base Exchange Capacity of Clays meq/l* | Base Exchange Capacity of Suspensions meq/l |
|---|---|---|---|---|
| [illegible]ments | 58 | 42.0 | 1,150 | 71.3 |
| [illegible] earth | 79 | 64.8 | 265 | 17.2 |
| [illegible]te | 238 | 74.0 | 87 | 6.4 |

[illegible] equivalents will be abbreviated meq

[illegible] base exchange capacities were important in relation to coagulation [illegible]. Also, the effects of coagulant dosage upon turbidity and [illegible] for the present study will be compared with similar effects [illegible] dosage in the alum coagulation study reported by Farmer [illegible], therefore, that the coagulant dosages used in both

...tigations be expressed in ... practice as ... of ... exchange capacity employed herein. These expressions appear in Table ...

TABLE 3

COAGULANT DOSAGES

| Ferric Sulfate | | Alum | |
|---|---|---|---|
| mg/l | µeq/l | mg/l | µeq/l |
| 3.0 | 34 | 5.0 | 45 |
| 5.0 | 57 | 15.0 | 135 |
| 50.0 | 570 | 100.0 | 900 |

...although maximum dosages of 5.0 mg/l were realized in both ... effective dosage of aluminum ion is considerably greater than that of the ferric ion because water of hydration constitutes a larger portion of the alum dosage. Probably the most meaningful comparisons between the two investigations can be made for dosages of (1) 5.0 mg/l of alum and 3.0 mg/l of ferric sulfate, (2) 5.0 mg/l of alum and 50 mg/l of ferric sulfate, and (3) 100 mg/l of alum and 50 mg/l of ferric sulfate. These combinations of dosages are not equal, but the two lower ferric sulfate concentrations bracket the lower alum dosage, and the highest dosages of the two studies represent concentrations greatly in excess of those necessary for good coagulation.

The choice of a satisfactory criterion of good coagulation is particularly difficult. Adequate coagulation must result in an extremely high degree of turbidity removal. The optical property, turbidity, ... can be relied upon as an index of removal efficiency. Use of this

[illegible] a given sample

An example of the manifestation of these effects has been presented in Table 2. The suspensions contain equal gravimetric concentrations of the three clays, but the turbidities they exhibit are widely divergent. For water treatment plant operation a practical criterion commonly used requires that the turbidity of coagulated and settled water be five units or less. Such a criterion is probably too stringent for use in this study because the short period of sedimentation was insufficient for the settling of the smaller particles which contribute most to the turbidity of a suspension. Moreover, the selection of a specific residual turbidity as the criterion would be to require a much larger removal efficiency for the kaolinite suspension (initial turbidity 294 units) than for the montmorillonite (initial turbidity 58 units).

Packham[28] has arbitrarily chosen as his coagulation criterion that dosage which reduces initial turbidity by 90 per cent. This choice is undesirable, because it differs so widely from acceptable conditions encountered in water treatment plant operation. We have arbitrarily chosen 90 per cent removal of initial turbidity as the criterion of satisfactory coagulation and results of the two studies will be compared on this basis.

The residual turbidities and particle mobilities for each combination of clay and coagulant dosage have been graphed as functions of pH. Both graphs for a single combination appear in the same figure. (The residual turbidities are expressed as percentages of the initial turbidity of each suspension.) Figures 5, 6, 7, and 8 are based upon

the turbidity and mobility results for [illegible] suspensions which were treated with 0, 3, 5, and 50 mg/l of [illegible] respectively.

In Fig. 5, pH is observed to exert minor influence upon montmorillonite mobility in the absence of any coagulant. Final turbidity is little affected by pH. Some turbidity removal was accomplished by the agitation and sedimentation of the jar test procedure, but the clarification so achieved was not significant.

Hannah's[40] electrophoretic studies revealed that the mobility of the suspended clay alone was relatively independent of pH, but the magnitude of the mobilities he reported were approximately 30 per cent smaller than those recorded during the present investigation. The latter agree much more closely with the maximum negative clay mobilities reported by Mattson[20] and by others than do Hannah's. Such agreement can not be interpreted to be a proof of accuracy, because Mattson, for example, worked with a different clay and did not report pH values. However, as consideration of figures below will indicate, the graph of the mobility versus pH for zero coagulant dosage does fairly well define the maximum negative mobilities observable for the suspensions and coagulant under consideration. In view of this relationship, comparison of mobilities for zero coagulant dosage with Mattson's maximum negative clay mobilities appears to be worthwhile.

The lack of agreement with Hannah's values led to a reconsideration of the equipment and procedure for mobility measurement. Of the mechanical devices which are used, the counter is the unit most probably capable of introducing an error of such size and consistency. The precision of the meters is about one or two per cent of the full scale

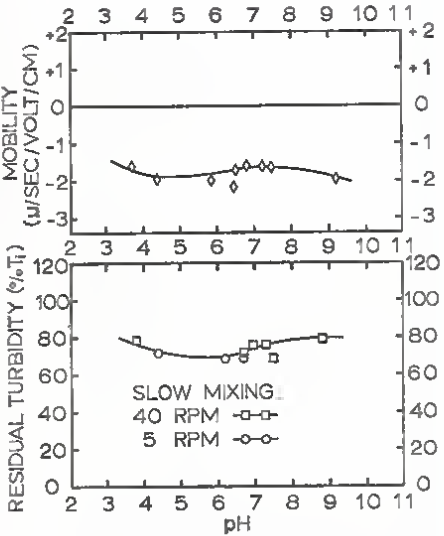


FIG. 5 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION. CLAY: MONTMORILLONITE FERRIC SULFATE DOSAGE: 0.0 MG / L

reading, and the accuracy is not likely to be as good as the precision. Under conditions such as the electrolyte conductivity or the available power supply voltage make it necessary to measure a current corresponding to only ten or fifteen per cent of the full scale reading, the error involved in the determination may be six to ten times as large as that for a reading at full scale. Perhaps the use of some more sensitive method of field intensity measurement circuitry would allow closer agreement among the results of independent investigators.

Fig. 6 shows the effect of pH upon mobility and turbidity removal in the montmorillonite clay suspension for the 3-mg/l coagulant dosage. Increasing pH was accompanied by a gradual increase in the magnitude of the negative mobility. The same trend was shown for Hannah's 3-mg/l dosage, and, as was previously mentioned, the magnitudes of the mobilities were only about 75 per cent of those from the present study. Whereas the only good coagulation resulting from that alum dose was perikinetic coagulation at pH less than 4.5, 3-mg/l of ferric sulfate yielded good coagulation from pH 5.5 to pH 6.6.

With an increase of ferric sulfate to 5 mg/l as shown in Fig. 7, the increase in mobility with increasing pH becomes greater, although the curve is not so smooth. The most noticeable effect of the increased coagulant dose is the broadening of the zone of good coagulation over the range pH 4.6 to 7.8.

The 50-mg/l ferric sulfate dosage resulted in charge reversal for values of pH less than 5.3. In Fig. 8, the algebraic decrease in mobility with increasing pH was observed again as it had been in the previous figures. Hannah's comparable alum dose of 100 mg/l resulted in a mobility curve of similar shape above pH 4.7, but the isoelectric

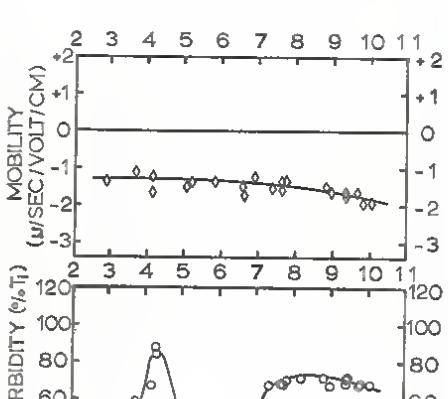


FIG. 6 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION. CLAY: MONTMORILLONITE FERRIC SULFATE DOSAGE. 3.0 MG / L

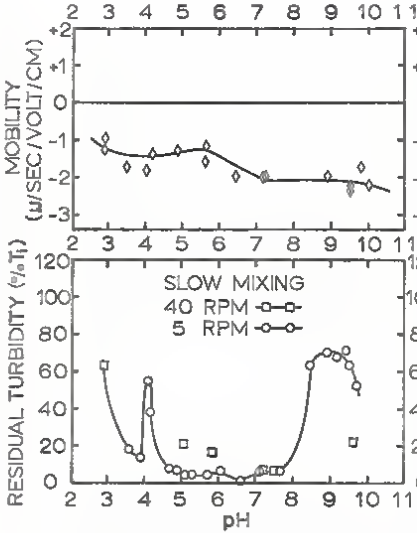


FIG. 7 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION. CLAY : MONTMORILLONITE FERRIC SULFATE DOSAGE : 5.0 MG / L

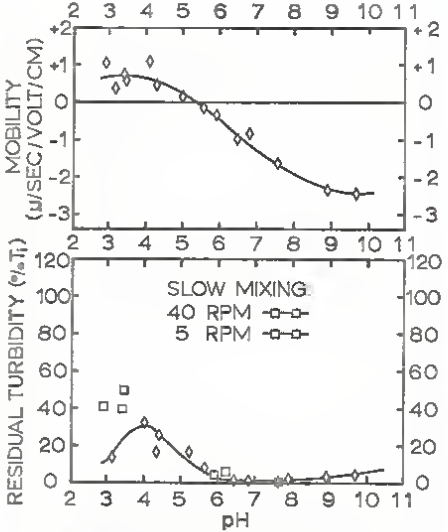


FIG 8 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION CLAY MONTMORILLONITE FERRIC SULFATE DOSAGE : 50 MG / L

alum (pH 6 6) [illegible] beauty of aluminum increased the charge reversal effect of the alum also decreased. The alum dose resulted in good perikinetic coagulation below pH 4.5 and both alum and ferric sulfate produced good orthokinetic coagulation from pH 5.5 to 8.8 and from 5 5 to 10.0 respectively.

Fig 9 is a composite of the four preceding figures. It allows ready comparison of the broadening of the zone of good coagulation with increasing coagulant dosage. Also the zone of perikinetic coagulation below pH 3 7 and the zone of poor or no coagulation from roughly pH 4 to pH 5 are easily identified. Probably the most important relationship graphically illustrated in the figure is that the isoelectric point occurring at pH 5.3 for the one dosage causing charge reversal marks the beginning of the pH zone of most economical coagulation of the particular clay and for the arbitrary good coagulation criterion chosen

The next series of figures pertain to the coagulation of fuller's earth. Fig 10 illustrates the effect of pH in the absence of coagulant. As was the case with montmorillonite, in the absence of coagulant, negative mobility increased with increasing pH value; Perikinetic coagulation occured below pH 4.2 although no such coagulation had been observed for montmorillonite.

Beginning with Fig. 11, the mobility curves become more complex as the varying effectiveness of the coagulants for charge reversal at different values of pH becomes more evident For the 3-mg/l dosage, the original particle charge is reversed over a pH range of slightly more than one unit. For this particular dose, comparison of mobility curve shapes for ferric and alum coagulation are virtually impossible because of lack of similarity. Good ferric coagulation was observed over the

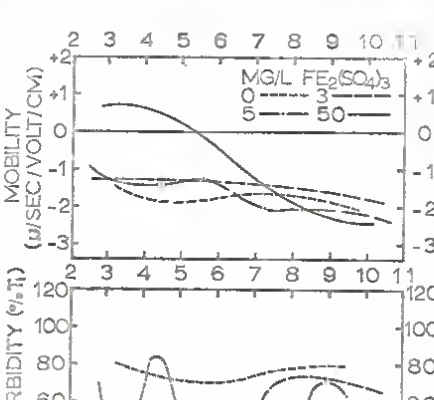


FIG 9 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION. CLAY : MONTMORILLONITE

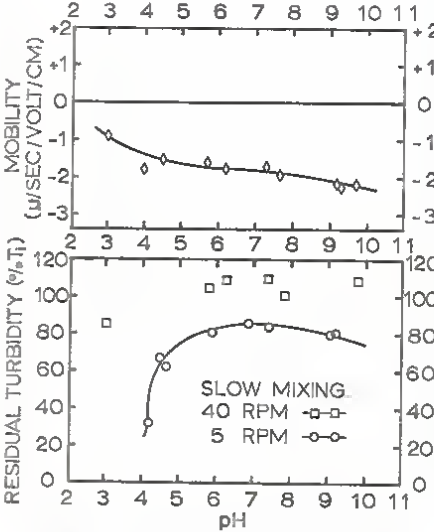


FIG. 10. - THE EFFECT OF pH AND MOBILITY UPON COAGULATION. CLAY: FULLER'S EARTH FERRIC SULFATE DOSAGE: 0.0 MG / L

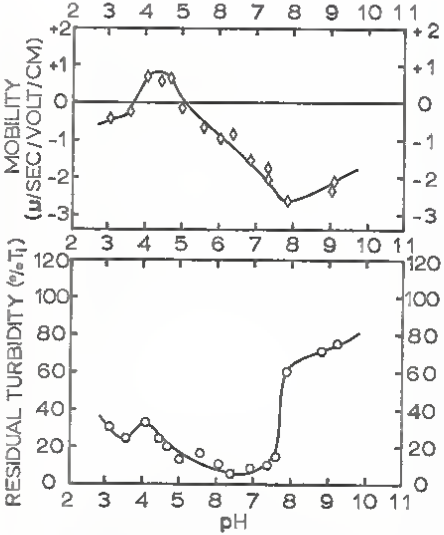


FIG 11 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION. CLAY : FULLER'S EARTH FERRIC SULFATE DOSAGE : 30 MG / L

pH range 5.6 to 7.5.

When the ferric sulfate dose was increased to 5 mg/l (Fig. 12) the zone of charge reversal was increased to 3 pH units, and good coagulation occurred above pH 5.5. A most interesting effect noted in this particular portion of the study is the greater efficiency of 5 rpm slow mixing for perikinetic coagulation and the better orthokinetic coagulation that accompanied the 40 rpm slow mixing.

The mobility curve for the 50-mg/l ferric sulfate dosage (Fig. 13) appears to be typical of excess ferric sulfate dosage for the three clays studied. Particles were positive below pH 6.3, were isoelectric at that point, and became increasingly negative as pH was raised to 10. The slope of the curve is steepest immediately above and below the isoelectric point which clearly indicates a zone of minimum stability. Ramaker's comparable alum curve changes less abruptly at the isoelectric point, and the apparent effect of increasing solubility at low pH is evident. Ferric coagulation is good above pH 4.2

The composite graph for fuller's earth (Fig. 14) clarifies the relationship between the isoelectric point of the overdosed suspensions and the beginning of the zone of efficient coagulation. As was the case for montmorillonite, it appears that the "overdosed isoelectric point" does mark that beginning. Also, the broadening of the zone of good coagulation with increasing dosage is evidenced.

Individual mobility and turbidity graphs for the kaolinite clay are shown in Figures 15, 16, 17, and 18, and Fig. 19 is the corresponding composite. The mobility curves are very similar to those for fuller's earth, and the comments above concerning the latter are qualitatively applicable. Regarding coagulation, the kaolinite is much more nearly

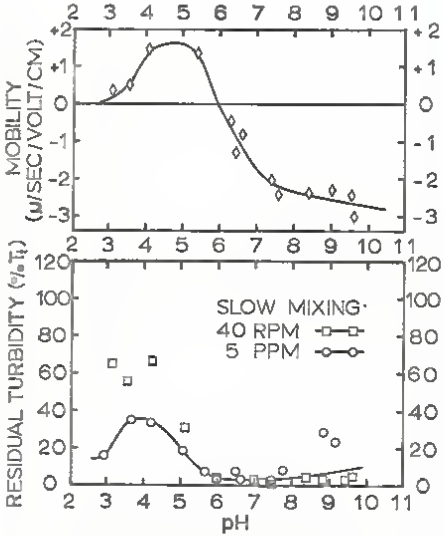


FIG 12 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION. CLAY; FULLER'S EARTH FERRIC SULFATE DOSAGE. 5.0 MG / L

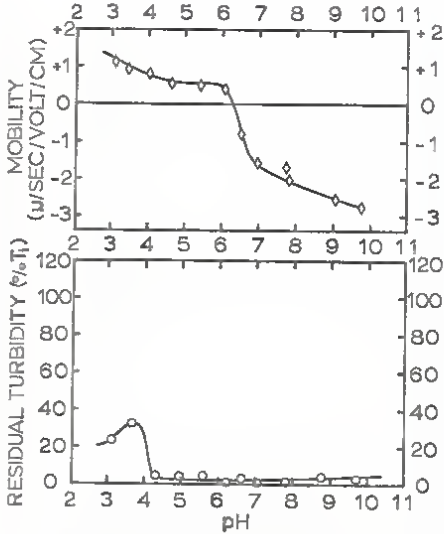


FIG 13. - THE EFFECT OF pH AND MOBILITY UPON COAGULATION CLAY : FULLER'S EARTH FERRIC SULFATE DOSAGE : 50 MG / L

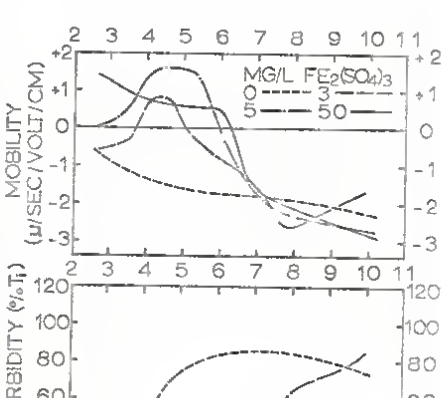


FIG. 14 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION CLAY - FULLER'S EARTH

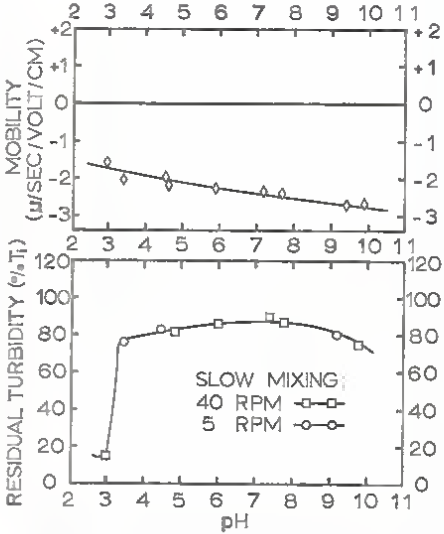


FIG. 15 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION. CLAY : KAOLINITE FERRIC SULFATE DOSAGE : 00 MG / L

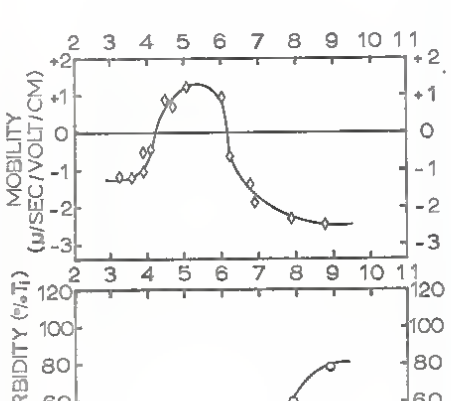


FIG.16 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION. CLAY : KAOLINITE FERRIC SULFATE DOSAGE : 30 MG / L

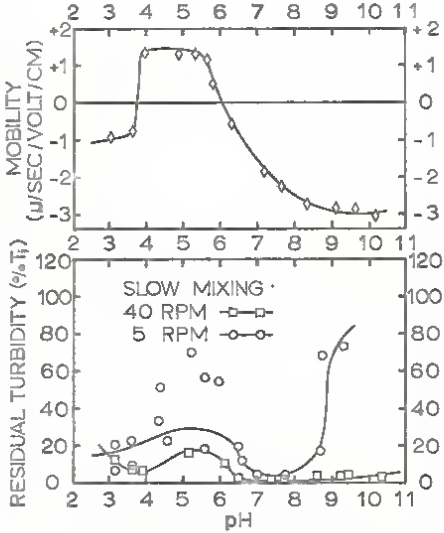


FIG 17 - THE EFFECT OF pH AND MOBILITY UPON COAGULATION. CLAY : KAOLINITE FERRIC SULFATE DOSAGE : 5.0 MG / L

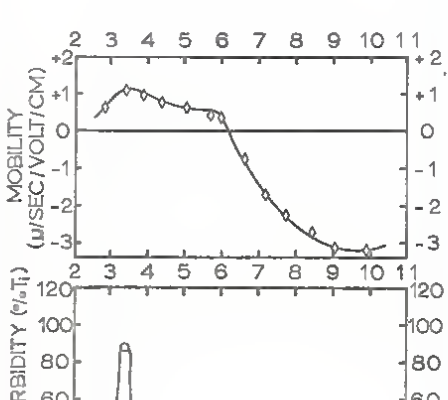


FIG 18 -THE EFFECT OF pH AND MOBILITY UPON COAGULATION
CLAY: KAOLINITE FERRIC SULFATE DOSAGE: 50. MG / L

FIG 19
VOLUME
CLAY - KAOLINITE

similar to the montmorillonite. Most important, however, is that the "overdosed isoelectric point" near pH 6.0 marks the beginning of the zone of good coagulation. Black and others[52] have shown that the same relationship between the "overdosed isoelectric point" and the zone of good coagulation exist for the ferric sulfate coagulation of natural colored waters.

An additional observation of possible importance concerns base exchange capacities of the suspensions. There was no observation of charge reversal in the present investigation for dosages for which the ratio of coagulant dose to base exchange capacity (both expressed in meq/l) was less than 1.0. Good coagulation occurred for all three clays, however, with a dosage of 3 mg/l. For this dose the ratio mentioned above for montmorillonite is 0.48, for fuller's earth is 2.0, and for kaolinite is 5.3. Work with ferric sulfate doses in a range which would yield ratios near unity should reveal more interesting information on charge reversal phenomena.

The U. S. Public Health Service[1] has set 0.3 mg/l of iron as the maximum allowable concentration of that constituent in drinking water. In the present research, therefore, determination of the residual iron content in the supernatant was necessary in order that suitability of the various treatments could be evaluated. The results of the determination are graphically presented in Figures 20 through 28.

The most important information obtained from the iron determination was that for all the pH zone of good coagulation, the residual iron content is below the maximum allowable concentration. Another interesting observation which is generally applicable for the ferric sulfate coagulation of the three clays is that residual iron values are less

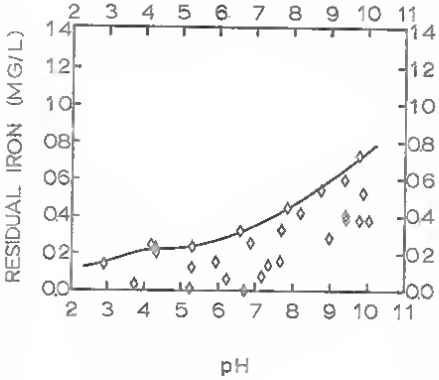


FIG 20 - THE EFFECT OF pH ON IRON RESIDUAL CLAY- MONTMORILLONITE FERRIC SULFATE DOSAGE 30 MG/L

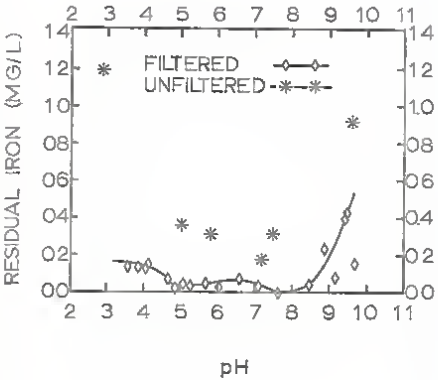


FIG 21 - THE EFFECT OF pH ON IRON RESIDUAL CLAY MONTMORILLONITE FERRIC SULFATE DOSAGE 5.0 MG/L

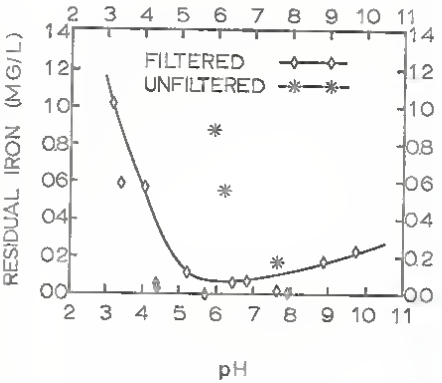


FIG 22 - THE EFFECT OF pH ON IRON RESIDUAL CLAY MONTMORILLONITE FERRIC SULFATE DOSAGE 50 MG/L

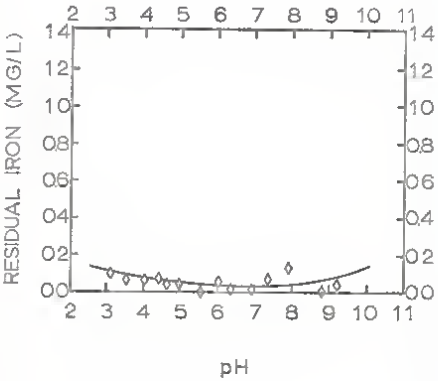


FIG 23- THE EFFECT OF pH ON IRON RESIDUAL CLAY FULLER'S EARTH FERRIC SULFATE DOSAGE 30 MG/L

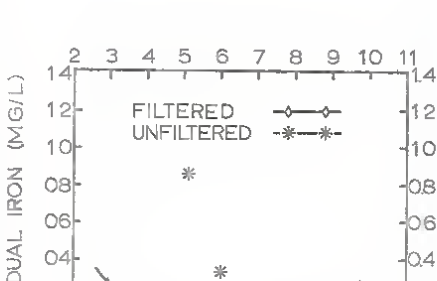


FIG 24 - THE EFFECT OF pH ON IRON RESIDUAL. CLAY. FULLER'S EARTH FERRIC SULFATE DOSAGE: 5.0 MG/L

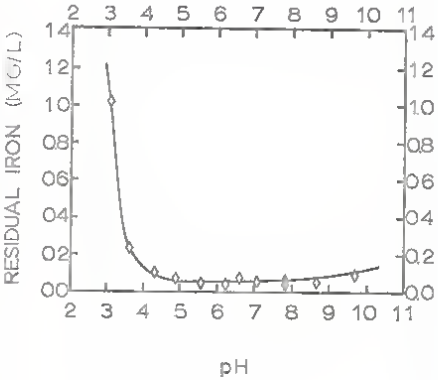


FIG 25 - THE EFFECT OF pH ON IRON RESIDUAL CLAY FULLER'S EARTH FERRIC SULFATE DOSAGE, 50 MG/L

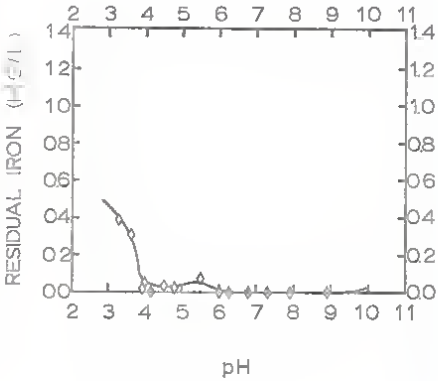


FIG 26.- THE EFFECT OF pH ON IRON RESIDUAL. CLAY KAOLINITE FERRIC SULFATE DOSAGE 3.0 MG/L

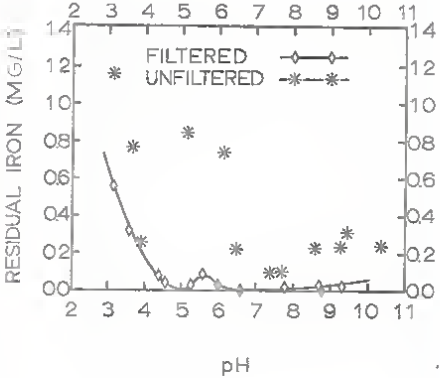


FIG 27 - THE EFFECT OF pH ON IRON RESIDUAL CLAY KAOLINITE FERRIC SULFATE DOSAGE 50 MG/L

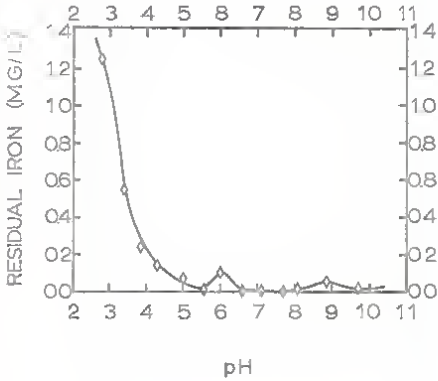


FIG 28- THE EFFECT OF pH ON IRON RESIDUAL CLAY. KAOLINITE FERRIC SULFATE DOSAGE. 50. MG/L

than the maximum allowable concentrations in the low pH range down to pH 3.8. Furthermore, even at pH 3.0 no supernatant contained more than 1 mg/l of iron in solution. These low residual iron values for clay coagulation are much lower than those reported for colored water coagulation.

Black and others[58] have reported residual iron values for comparable coagulant dosages in colored water that are six times as large as the largest observed in the present study for the same pH of 3.0. At pH values up to 4 or 5, the ratio was even larger. The difference in behavior of the clay and color colloids in this respect point out the need for a more thorough understanding of basic coagulation mechanisms.

For the present research it was necessary to determine whether the pH of the samples employed for mobility determinations were identical with the pH of the corresponding jar test suspensions. Figures 29, 30, 31, and 32 show the close agreement between the respective pH values. Fig. 33 is a composite of the four, which shows the effect of coagulant dosage upon the value of pH. It should be remembered that the suspensions which were used were synthetic preparations containing 50 mg/l of sodium bicarbonate. A more poorly buffered solution might not yield such agreement between the two. Even with the systems used it was difficult to dose the suspensions with the exact quantities of acid or base required to obtain evenly spaced mobility and turbidity curve points. Only the curves for Fuller's earth are shown, since these for the other clays were similar.

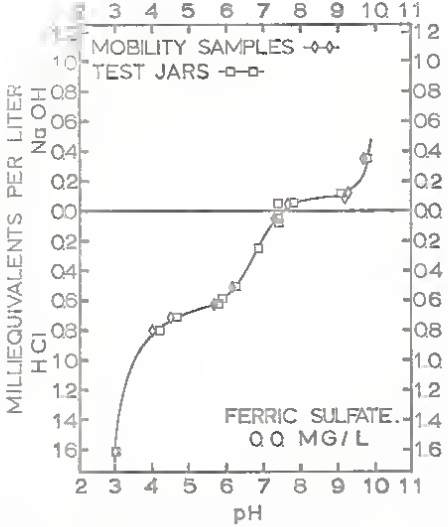
MOBILITY SAMPLES
TEST JARS
FERRIC SULFATE.
0.0 MG/L
MILLIEQUIVALENTS PER LITER
NaOH
HCl
pH
2 3 4 5 6 7 8 9 10 11
1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6

FIG 29 - QUANTITIES OF ACID OR BASE REQUIRED FOR pH ADJUSTMENT OF FULLER'S EARTH.

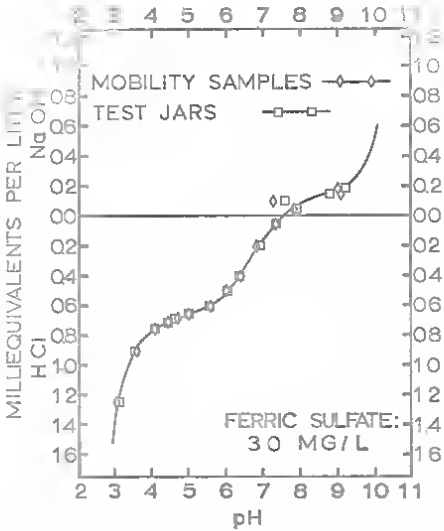
MOBILITY SAMPLES
TEST JARS
FERRIC SULFATE:
30 MG/L
MILLIEQUIVALENTS PER LITER
Na OH
H Cl
pH
2 3 4 5 6 7 8 9 10 11
10 08 06 04 02 00 02 04 06 08 10 12 14 16

FIG 30 - QUANTITIES OF ACID OR BASE REQUIRED FOR pH ADJUSTMENT OF FULLER'S EARTH.

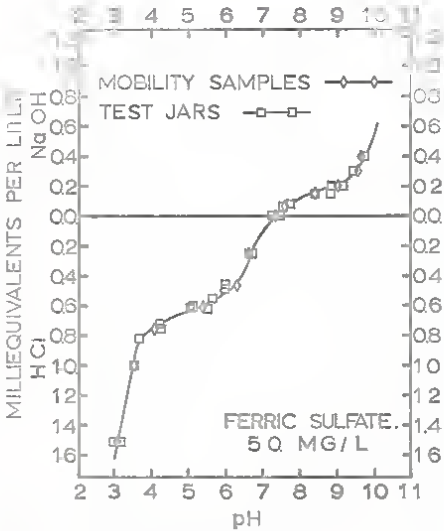


FIG 31 - QUANTITIES OF ACID OR BASE REQUIRED FOR pH ADJUSTMENT OF FULLER'S EARTH.

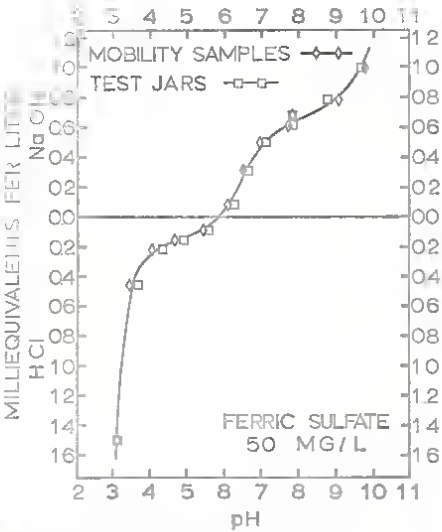


FIG 32 - QUANTITIES OF ACID OR BASE REQUIRED FOR pH ADJUSTMENT OF FULLER'S EARTH

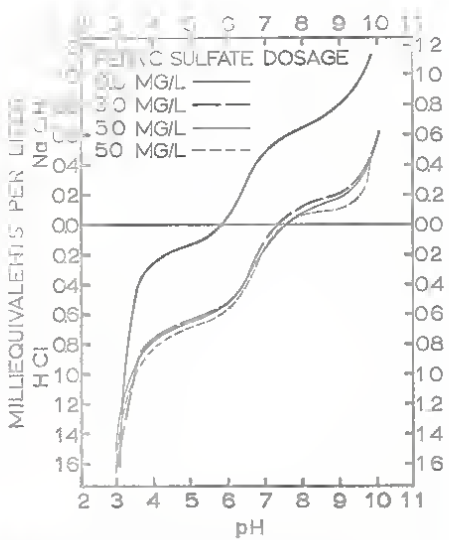


FIG 33 - QUANTITIES OF ACID OR BASE REQUIRED FOR pH ADJUSTMENT OF FULLER'S EARTH

## VII CONCLUSIONS

In the present investigation, charge reversal at low pH was observed for all three clay suspensions when the ratio of coagulant dosage to base exchange capacity (both expressed in meq/l) exceeded three. With increasing pH the mobilities of these suspensions decreased until the isoelectric point (in the pH range 5 - 7) occurred. This "overdosed isoelectric point" was found to mark the beginning of the zone of efficient orthokinetic coagulation of all three of the suspensions studied. Such behavior has been reported for the coagulation of colored water with ferric sulfate by Black and others.[32] Furthermore, an analysis of the results of clay coagulation with alum reported by Hannah[40] revealed that the "overdosed isoelectric point" was an indicator of effective coagulation conditions for these suspensions.

The base exchange capacities of the suspensions studied were not found to be directly or proportionally related to the coagulant dosages required to effect satisfactory coagulation, but they did significantly affect the coagulant dosages required to cause charge reversal at low pH.

For all of the combinations of ferric sulfate dosages and clay suspensions studied, it was observed that in the pH zones of good coagulation the residual iron values were less than the maximum allowed in drinking water by the U. S. Public Health Service.[1] Moreover, even at low pH the residual iron values were less (by a factor of six to ten) than those reported by Black and others[32] for the coagulation of colored

water with comparable dosages of ferric sulfate. The difference between the behavior of the colored and turbid waters mentioned above may be caused by the ability of organic matter (including organic color) present in the water to form complexes with both ferrous and ferric ions.

The conclusion of greatest practical importance resulting from the present investigation is that the microelectrophoretic technique may be useful for the prediction of the pH zone of most effective coagulation of natural, turbid water. Further study is necessary to determine whether there is an "overdosed isoelectric point" for natural, turbid waters which marks the zone of good orthokinetic coagulation.

# APPENDIX

TABLE 4

EFFECT OF pH ON ELECTROPHORETIC MOBILITY AND SEDIMENTATION OF MONTMORILLONITE CLAY

| Jar No. | NCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility $\mu$/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity |
|---|---|---|---|---|---|---|---|
| 1 | 0.61 | | 3.72 | -1.58 | 3.80 | 45 | 78 |
| 2 | 0.31 | | 6.51 | -1.69 | 6.69 | 42 | 72 |
| 3 | 0.26 | | 6.79 | -1.58 | 6.95 | 44 | 76 |
| 4 | 0.02 | | 7.22 | -1.60 | 7.30 | 44 | 76 |
| 5 | | 0.02 | 7.44 | -1.66 | 7.52 | 40 | 69 |
| 6 | | 0.18 | 9.20 | -1.94 | 8.80 | 46 | 79 |
| 181A | 0.55 | | 5.85 | -1.98 | 6.20 | 40 | 69 |
| 182A | 0.40 | | 6.46 | -2.16 | 6.70 | 40 | 69 |
| 187 | 0.70 | | 4.40 | -1.94 | | 42 | 72 |

*Turbidity of initial suspension: 58. No coagulant used for this series.

TABLE 5

COAGULATION OF MONTMORILLONITE CLAY WITH 3.0 MILLIGRAMS PER LITER OF [illegible] SILICA

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility $\mu$/sec/v/cm | Final pH of Coagulated Water | Final[A] Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 85 | 0.00 | 0.00 | 7.37 | -1.55 | 7.36 | 39 | 68 | 0.14 |
| 86 | | 0.07 | 7.66 | -1.57 | 7.66 | 40 | 69 | 0.21 |
| 87 | | 0.20 | 8.93 | -1.67 | 8.96 | 39 | 68 | 0.70 |
| 88 | | 0.30 | 9.35 | -1.61 | 9.40 | 40 | 69 | 0.41 |
| 89 | | 0.40 | 9.80 | -1.93 | 9.75 | 39 | 68 | 0.38 |
| 90 | | 0.60 | 10.01 | -1.91 | 10.06 | 40 | 69 | 0.38 |
| 91 | 0.55 | | | | 6.22 | 6 | 10 | 0.07 |
| 92 | 0.30 | | | | 6.99 | 9 | 16 | --- |
| 93 | 0.25 | | | | 7.38 | 6 | 10 | 0.08 |
| 94 | | 0.07 | | | 8.20 | 42 | 72 | 0.42 |
| 95 | | 0.20 | | | 9.44 | 42 | 72 | 0.39 |
| 96 | | 0.30 | | | 9.87 | 42 | 72 | 0.53 |

TABLE 5 - CONTINUED

| Jar No. | HCl mg/l | NaOH mg/l | pH of Mobility Sample | Mobility $\mu$/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 109 | 0.15 | | 6.90 | -1.29 | 6.88 | 26 | 45 | 0.26 |
| 110 | | 0.05 | 7.62 | -1.37 | 7.70 | 40 | 69 | 0.33 |
| 111 | | 0.12 | 7.77 | -1.36 | 7.87 | 41 | 71 | 0.45 |
| 112 | | 0.18 | 8.81 | -1.50 | 8.78 | 42 | 72 | 0.54 |
| 113 | | 0.25 | 9.36 | -1.76 | 9.38 | 41 | 71 | 0.60 |
| 114 | | 0.35 | 9.65 | -1.87 | 9.77 | 40 | 69 | 0.73 |
| 115 | 1.30 | | 2.91 | -1.37 | 2.92 | 10 | 17 | 0.14 |
| 116 | 0.80 | | 3.68 | -1.10 | 3.73 | 34 | 59 | 0.04 |
| 117 | 0.70 | | 4.13 | -1.21 | 4.20 | 39 | 68 | 0.25 |
| 118 | 0.60 | | 5.21 | -1.39 | 5.31 | 14 | 24 | 0.24 |
| 119 | 0.50 | | 5.82 | -1.38 | 5.94 | 5 | 9 | 0.16 |
| 120 | 0.25 | | 6.58 | -1.51 | 6.60 | 15 | 26 | 0.35 |
| 157 | 0.68 | | 4.14 | -1.68 | 4.31 | 51 | 88 | 0.23 |

TABLE 5 - CONTINUED

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility μ/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 138 | 0.60 | | 5.07 | -1.54 | 5.25 | 7 | 12 | 0.01 |
| 139 | 0.35 | | 6.61 | -1.75 | 6.72 | 7 | 12 | 0.00 |
| 190 | 0.68 | | | | 4.33 | 49 | 85 | 0.21 |
| 191 | 0.60 | | | | 5.31 | 10 | 17 | 0.13 |

*Turbidity of initial suspension: 58.

TABLE 6

COAGULATION OF MONTMORILLONITE CLAY WITH 5.0 MILLIGRAMS PER LITER OF FERRIC SULFATE

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility $\mu$/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 25 | 1.70 | | 2.92 | -0.93 | 2.90 | 37 | 64 | 1.19 |
| 26 | 0.60 | | 4.87 | -1.27 | 5.06 | 12 | 21 | 0.37 |
| 27 | 0.53 | | 5.62 | -1.17 | 5.85 | 10 | 17 | 0.32 |
| 28 | 0.00 | 0.00 | 7.15 | -1.78 | 7.20 | 4 | 7 | 0.18 |
| 29 | | 0.14 | 7.22 | -1.78 | 7.50 | 4 | 7 | 0.32 |
| 30 | | 0.60 | 10.00 | -2.20 | 9.61 | 13 | 22 | 0.92 |
| 55 | 0.68 | | 3.89 | -1.22 | 3.89 | 8 | 14 | 0.14 |
| 56 | 0.59 | | 4.19 | -1.35 | 4.13 | 22 | 38 | 0.15 |
| 57 | 0.25 | | 6.46 | -1.77 | 6.58 | 1 | 2 | 0.08 |
| 58 | | 0.20 | 8.90 | -1.75 | 8.90 | 41 | 71 | 0.24 |
| 59 | | 0.30 | 9.49 | -2.37 | 9.42 | 42 | 72 | 0.40 |
| 60 | | 0.40 | 9.79 | -1.80 | 9.69 | 31 | 53 | 0.16 |
| 153 | 0.90 | | 3.52 | -1.72 | 3.58 | 11 | 19 | 0.14 |

TABLE 6 - CONTINUED

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility $\mu$/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 154 | 0.70 | | 4.03 | -1.80 | 4.11 | 32 | 55 | 0.11 |
| 155 | 0.55 | | 5.61 | -1.37 | 5.68 | 3 | 5 | 0.05 |
| 156 | | 0.28 | 9.49 | -2.26 | 9.47 | 37 | 64 | 0.43 |
| 176 | | 0.22 | | | 9.17 | 40 | 69 | 0.09 |
| 177 | | 0.12 | | | 8.46 | 37 | 64 | 0.05 |
| 178 | 0.00 | 0.00 | | | 7.65 | 4 | 7 | 0.00 |
| 192 | 0.62 | | | | 4.69 | 5 | 9 | 0.07 |
| 193 | 0.50 | | | | 5.10 | 3 | 5 | 0.05 |
| 194 | 0.48 | | | | 6.06 | 4 | 7 | 0.03 |
| 195 | 0.10 | | | | 7.12 | 4 | 7 | 0.04 |
| 208 | 0.62 | | | | 4.87 | 4 | 7 | 0.02 |
| 209 | 0.59 | | | | 5.30 | 3 | 5 | 0.04 |

*Turbidity of initial suspension: 58.

TABLE 7

COAGULATION OF MONTMORILLONITE CLAY WITH 50 MILLIGRAMS PER LITER OF FERRIC SULFATE

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility $\mu$/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 19 | 1.70 | | 2.90 | +3.03 | 2.90 | 24 | 41 | 9.8 |
| 20 | 0.60 | | 3.40 | +0.71 | 3.40 | 23 | 40 | 3.1 |
| 21 | 0.53 | | 3.47 | +0.38 | 3.45 | 29 | 50 | 3.7 |
| 22 | 0.00 | 0.00 | 5.56 | -0.17 | 5.90 | 3 | 5 | 0.88 |
| 23 | | 0.07 | 5.91 | -0.34 | 6.20 | 4 | 7 | 0.56 |
| 24 | | 0.60 | 7.57 | -1.65 | 7.63 | 1 | 2 | 0.18 |
| 61 | 1.30 | | 3.17 | +0.38 | 3.15 | 8 | 14 | 1.02 |
| 62 | 0.25 | | 4.10 | +1.07 | 4.03 | 19 | 33 | 0.57 |
| 63 | | 0.25 | 6.46 | -0.09 | 6.44 | 1 | 2 | 0.06 |
| 64 | | 0.40 | 6.78 | -0.85 | 6.82 | 1 | 2 | 0.07 |
| 65 | | 0.75 | 8.87 | -2.37 | 8.86 | 3 | 5 | 0.18 |
| 66 | | 1.00 | 9.87 | -2.43 | 9.72 | 3 | 5 | 0.24 |

TABLE 7 - CONTINUED

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility μ/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 151 | 0.18 | | 4.30 | +0.67 | 4.41 | 18 | 31 | 0.03 |
| 152 | 0.08 | | 4.95 | +0.16 | 5.22 | 10 | 17 | 0.12 |
| 202 | 0.42 | | | | 3.39 | 135 | 233 | 0.59 |
| 203 | 0.15 | | | | 4.37 | 10 | 17 | 0.05 |
| 204 | 0.00 | 0.00 | | | 5.67 | 5 | 9 | 0.00 |
| 205 | | 0.60 | | | 7.62 | 1 | 2 | 0.02 |
| 206 | | 0.65 | | | 7.91 | 2 | 3 | 0.01 |

*Turbidity of initial suspension: 58.

TABLE 8

EFFECT OF pH ON ELECTROPHORETIC MOBILITY AND SEDIMENTATION OF FULLER'S EARTH

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility μ/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity |
|---|---|---|---|---|---|---|---|
| 7 | 1.62 | | 3.00 | -0.89 | 3.00 | 67 | 85 |
| 8 | 0.62 | | 5.70 | -1.60 | 5.80 | 83 | 105 |
| 9 | 0.51 | | 6.18 | -1.78 | 6.25 | 86 | 109 |
| 10 | 0.05 | | 7.28 | -1.72 | 7.37 | 87 | 110 |
| 11 | | 0.05 | 7.65 | -1.94 | 7.80 | 81 | 101 |
| 12 | | 0.35 | 9.70 | -2.16 | 9.75 | 86 | 109 |
| 183 | 0.80 | | 4.00 | -1.50 | 4.18 | 26 | 33 |
| 184 | | 0.12 | 9.29 | -2.29 | 9.06 | 63 | 80 |
| 185 | 0.72 | | 4.49 | -1.53 | | 53 | 67 |
| 189 | | 0.09 | 9.18 | -2.13 | | 64 | 81 |
| 214 | 0.72 | | | | 4.66 | 49 | 62 |
| 215 | 0.58 | | | | 5.90 | 64 | 81 |

TABLE 8 - CONTINUED

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility μ/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity |
|---|---|---|---|---|---|---|---|
| 216 | 0.25 | | | | 6.86 | 58 | 86 |
| 219 | 0.08 | | | | 7.41 | 66 | 84 |

*Turbidity of initial suspension: 58. No coagulant used for this series.

TABLE 9

COAGULATION OF FULLER'S EARTH WITH 3.0 MILLIGRAMS PER LITER OF FERRIC SULFATE

| Jar No. | KCl meq/l | NaCN meq/l | pH of Mobility Sample | Mobility $\mu$/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 121 | 1.25 | | 3.07 | -0.46 | 3.12 | 24 | 30 | 0.10 |
| 122 | 0.90 | | 3.60 | -0.26 | 3.54 | 19 | 24 | 0.07 |
| 123 | 0.75 | | 4.07 | +0.68 | 4.07 | 26 | 33 | 0.07 |
| 124 | 0.70 | | 4.45 | +0.55 | 4.43 | 19 | 24 | 0.08 |
| 125 | 0.68 | | 4.70 | +0.63 | 4.67 | 15 | 19 | 0.05 |
| 126 | 0.65 | | 5.00 | -0.17 | 4.99 | 10 | 13 | 0.05 |
| 127 | 0.60 | | 5.58 | -0.66 | 5.56 | 13 | 16 | 0.00 |
| 128 | 0.50 | | 6.05 | -0.98 | 6.03 | 8 | 10 | 0.06 |
| 129 | 0.40 | | 6.38 | -0.84 | 6.38 | 4 | 5 | 0.02 |
| 130 | 0.20 | | 6.82 | -1.54 | 6.92 | 6 | 8 | 0.02 |
| 131 | 0.05 | | 7.34 | -2.08 | 7.36 | 8 | 10 | 0.06 |
| 132 | | 0.05 | 7.87 | -2.62 | 7.90 | 47 | 60 | 0.14 |

TABLE 9 - CONTINUED

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility μ/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 160 | | 0.18 | 9.03 | -2.38 | 9.21 | 59 | 75 | 0.05 |
| 161 | | 0.10 | 7.32 | -1.74 | 7.50 | 11 | 14 | 0.00 |
| 175 | | 0.15 | 9.09 | -2.10 | 8.80 | 56 | 71 | 0.01 |

*Turbidity of initial suspension 79.

TABLE 10

COAGULATION OF FULLER'S EARTH WITH 5.0 MILLIGRAMS PER LITER OF FERRIC SULFATE

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility μ/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 31 | 1.52 | | 3.10 | +0.36 | 3.15 | 51 | 65 | 1.60 |
| 32 | 0.60 | | 5.40 | +1.38 | 5.12 | 25 | 32 | 0.86 |
| 33 | 0.46 | | 6.30 | -0.43 | 6.00 | 4 | 5 | 0.34 |
| 34 | 0.00 | 0.00 | 7.40 | -2.02 | 7.25 | 2 | 3 | 0.18 |
| 35 | | 0.07 | 7.57 | -2.41 | 7.52 | 1 | 1 | 0.16 |
| 36 | | 0.40 | 9.62 | -3.00 | 9.73 | 4 | 5 | 0.26 |
| 49 | 1.00 | | 3.54 | +0.68 | 3.34 | 44 | 56 | 0.16 |
| 50 | 0.75 | | 4.09 | +1.45 | 4.24 | 53 | 67 | 0.12 |
| 51 | 0.25 | | 6.62 | -0.80 | 6.99 | 3 | 4 | 0 08 |
| 52 | | 0.15 | 8.40 | -2.36 | 8.38 | 4 | 5 | 0.06 |
| 53 | | 0.20 | 9.02 | -2.30 | 8.82 | 3 | 4 | 0.08 |
| 54 | | 0.30 | 9.55 | -2.41 | 9.41 | 3 | 4 | 0.08 |

TABLE 10 - CONTINUED

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility μ/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 162 | 0.62 | | 6.42 | -1.28 | 6.52 | 6 | 8 | 0.00 |
| 196 | 1.52 | | | | 2.96 | 13 | 16 | 0.27 |
| 197 | 0.82 | | | | 3.66 | 28 | 35 | 0.05 |
| 198 | 0.62 | | | | 5.08 | 15 | 19 | 0.05 |
| 199 | 0.55 | | | | 5.66 | 6 | 8 | 0.05 |
| 201 | 0.25 | | | | 6.62 | 3 | 4 | 0.02 |
| 200 | 0.48 | | | | 6.00 | 3 | 4 | 0.03 |
| 207 | | 0.08 | | | 7.77 | 6 | 8 | 0.00 |
| 210 | | 0.15 | | | 8.82 | 23 | 29 | 0.00 |
| 211 | | 0.20 | | | 9.16 | 19 | 24 | 0.06 |
| 213 | 0.00 | | | | 7.43 | 3 | 4 | |
| 219 | 0.72 | | | | 4.22 | 27 | 34 | |

*Turbidity of initial suspension: 79.

TABLE 11

COAGULATION OF FULLER'S EARTH WITH 50 MILLIGRAMS [illegible]

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility μ/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity | Residual Iron mg/l |
|---|---|---|---|---|---|---|---|---|
| 67 | 1.50 | | 3.08 | +1.12 | 3.08 | 18 | 23 | 1.02 |
| 68 | 0.45 | | 3.42 | +0.92 | 3.62 | 26 | 33 | 0.24 |
| 69 | 0.22 | | 4.01 | +0.81 | 4.32 | 3 | 4 | 0.10 |
| 70 | 0.15 | | 4.63 | +0.55 | 4.91 | 3 | 4 | 0.07 |
| 71 | 0.08 | | 5.40 | +0.51 | 5.56 | 4 | 5 | 0.05 |
| 72 | | 0.08 | 6.08 | +0.38 | 6.22 | 1 | 1 | 0.05 |
| 79 | | 0.32 | 6.50 | -0.82 | 6.61 | 2 | 3 | 0.08 |
| 80 | | 0.50 | 6.93 | -1.58 | 7.05 | 1 | 1 | 0.06 |
| 81 | | 0.62 | 7.73 | -1.71 | 7.82 | 1 | 1 | 0.04 |
| 82 | | 0.68 | 7.81 | -2.05 | 7.82 | 1 | 1 | 0.05 |
| 83 | | 0.78 | 9.06 | -2.58 | 8.77 | 3 | 4 | 0.06 |
| 84 | | 1.00 | 9.75 | -2.74 | 9.68 | 2 | 3 | 0.10 |

*Turbidity of initial suspension 79.

TABLE 12

EFFECT OF pH ON ELECTROPHORETIC MOBILITY AND SEDIMENTATION OF KAOLINITE CLAY

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility $\mu$/sec/v/cm | Final pH of Coagulated Water | Final* Turbidity | Final Turbidity as Per Cent of Initial Turbidity |
|---|---|---|---|---|---|---|---|
| 13 | 1.62 | | 2.95 | -1.55 | 2.92 | 43 | 15 |
| 14 | 0.62 | | 4.65 | -2.19 | 4.81 | 253 | 82 |
| 15 | 0.51 | | 5.90 | -2.26 | 6.00 | 255 | 87 |
| 16 | 0.05 | | 7.20 | -2.32 | 7.58 | 266 | 90 |
| 17 | | 0.05 | 7.68 | -2.40 | 7.75 | 257 | 87 |
| 18 | | 0.35 | 9.89 | -2.67 | 9.76 | 220 | 75 |
| 145 | 0.65 | | 4.57 | -1.56 | 4.86 | 245 | 83 |
| 185 | 1.00 | | 3.40 | -2.02 | 3.45 | 225 | 76 |
| 186 | | 0.15 | 9.42 | -2.70 | 9.22 | 235 | 80 |

*Turbidity of initial suspension: 294. No coagulant used for this series.

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mobility Sample | Mobility $\mu$/sec/v/cm | Ex. A pt. of Dosage cu Wat | Final Turbidity | Fir... as I... Init... | ... |
|---|---|---|---|---|---|---|---|---|
| 133 | 1.25 | | 3.26 | -1.19 | 3.23 | 46 | 16 | 0.00 |
| 134 | 0.90 | | 3.39 | -1.22 | 3.62 | 56 | 19 | 0.30 |
| 135 | 0.75 | | 3.93 | -1.02 | 3.96 | 69 | 23 | 0.05 |
| 136 | 0.70 | | 4.11 | -0.46 | 4.17 | 51 | 17 | 0.00 |
| 137 | 0.65 | | 4.48 | +0.92 | 4.53 | 6[illegible] | 7[illegible] | 0.0[illegible] |
| 138 | 0.60 | | 5.13 | +1.21 | 5.49 | 1[illegible] | 3[illegible] | 0.[illegible] |
| 139 | 0.50 | | 6.01 | +0.96 | 5.98 | 1[illegible] | [illegible] | [illegible] |
| 140 | 0.40 | | 6.22 | -0.63 | 6.26 | 44 | 1[illegible] | [illegible] |
| 141 | 0.20 | | 6.79 | -1.38 | 6.81 | 25 | [illegible] | [illegible] |
| 142 | 0.00 | | 6.89 | -1.89 | 7.30 | 46 | 16 | [illegible] |
| 143 | | 0.05 | 7.88 | -2.29 | 7.92 | 175 | 60 | 0.0 |
| 144 | | 0.12 | 8.77 | -2.48 | 8.90 | 230 | 78 | 0.00 |

TABLE 13 - CONTINUED

| Jar No. | HCl meq/l | F C req/l | pH of [illegible] 5 min | [illegible] µ/cc / / | [illegible] | Flo [illegible] | [illegible] | [illegible] | [illegible] |
|---|---|---|---|---|---|---|---|---|---|
| 146 | 0.72 | | 3.96 | 0.1 | [illegible] | 49 | 0 | [illegible] | |
| 147 | 0.62 | | 4.71 | 10 [illegible] | 4.60 | 65 | 0 | [illegible] | |

*Turbidity of initial suspension: [illegible]

| [illegible] | [illegible] mg/l | [illegible] mg/l | [illegible] of Nobulin Sample | [illegible] g/cm³ | [illegible] ml of [illegible] Water | Final Turbid[illegible] | [illegible] | [illegible] |
|---|---|---|---|---|---|---|---|---|
| 140 | 0.62 | | 5.33 | 0.8 | 4.[illegible] | 6[illegible] | [illegible] | [illegible] |
| 1[illegible] | 0.55 | | [illegible].60 | 1.17 | 5.2 | 5[illegible] | [illegible] | [illegible] |
| 1[illegible] | [illegible].51 | | | | 3.35 | 59 | [illegible] | [illegible] |
| 1[illegible] | [illegible].[illegible] | | | | [illegible] | [illegible] | [illegible] | [illegible] |
| 1[illegible] | [illegible] | | | | [illegible] | [illegible] | [illegible] | [illegible] |
| 1[illegible] | [illegible] | | | | [illegible] | [illegible] | [illegible] | [illegible] |
| 1[illegible] | [illegible] | | | | 5.51 | 1[illegible] | [illegible] | [illegible] |
| 1[illegible] | 0.[illegible]5 | | | | 6.59 | 32 | [illegible] | [illegible] |
| 1[illegible] | 1.5 | | | | 3.1[illegible] | 17 | [illegible] | |
| 170 | 0.[illegible] | | | | 3.6 | 25 | [illegible] | |
| 171 | 0.[illegible]9 | | | | 4.5[illegible] | 96 | [illegible] | |
| 172 | 0.69 | | | | 5.60 | 164 | 50 | |
| 173 | 0.5[illegible] | | | | 6.47 | 37 | 19 | |

TABLE 34 -- CONTD.

| | | |

| Jar No. | HCl meq/l | NaOH meq/l | pH of Mixture | [illegible] | [illegible] of Coagulation | Final Turbidity | [illegible] | [illegible] |
|---|---|---|---|---|---|---|---|---|
| /3 | 1.5 | | [illegible] | 2.6 | [illegible] | 25 | 7 | [illegible] |
| /4 | 0.45 | | [illegible] | 3.43 | [illegible] | 90 | 86 | [illegible] |
| / | 0.27 | | [illegible] | 0.0 | 3.57 | 25 | 9 | 0.24 |
| /6 | 0.15 | | 4.3[illegible] | 10.77 | [illegible] | 15 | 5 | 0.14 |
| 77 | 0.08 | | [illegible].07 | 40.60 | 5.01 | 3 | 3 | 0.07 |
| 78 | | 0.03 | 5.90 | 40.39 | 6.00 | 2 | 1 | 0.10 |
| 103 | | 0.30 | 6.60 | -0.77 | 6.6[illegible] | 3 | 1 | 0.01 |
| 104 | | 0.50 | 7.17 | -1.70 | 7.12 | 2 | 1 | 0.01 |
| 105 | | 0.69 | 7.70 | -2.2[illegible] | 7.70 | 3 | 1 | 0.00 |
| 106 | | 0.88 | 8.41 | -2.73 | 8.10 | 4 | 1 | 0.02 |
| 107 | | 0.75 | 9.07 | -3.14 | 8.86 | 7 | 2 | 0.06 |
| 108 | | 1.00 | 9.88 | -3.16 | 9.70 | 8 | 3 | 0.02 |

TABLE 25 - CONTINUED

# BIBLIOGRAPHY

1. Publ. Health Service Drinking Water Standards, 1962. Pub. No. USPHS, Washington, D. C. (1962).

2. USPHS Drinking Water Standards, 1962. Federal Register (Mar. 6, 1962). p. 2152.

3. U. S. Public Health Service, Drinking Water Standards, 1961. Jour. AWWA, 53:935 (Aug. 1961).

4. Black, A. P. and Harmah, S. A. Electrokinetic Studies of Turbidity Removal by Coagulation With Aluminum Sulfate. Jour. AWWA, 53 438 (Apr. 1961).

5. Water Quality and Treatment. AWWA, New York, N. Y. (2nd ed., 1950). p. 131.

6. Packham, R. F. The Theory of the Coagulation Process - A Survey of the Literature. 2. Coagulation as a Water Treatment Process. Proc. of the Soc. for Water Treatment and Examination, 11:106 (1962).

7. D'Arcet, F. Note Relative to the Clarification of the Water of the Nile and Water in General Which Holds Earthly Substances in Suspension. (Articles from French Journals Translated by J. Orderson). J. Franklin Instr., Last Series, 22 256 (1838).

8. Jaunet, M. C. Monit. Sci., 7 1007 (1865).

9. Austen, P. T. and Wilbur, F. A. Report of the Purification of Drinking Water by Alum. Annual Report of the State Geologist of New Jersey, 1884. Trenton (1885). p. 142.

10. Fuller, G. W. Water Purification at Louisville. Van Nostrand Co., New York (1898).

11. Hill, E. V. Manufacture and Use of Chlorinated Copperas. Proc. of Indiana Water Supply Assn. (1912). p. 119.

12. Hedgepath, L. L. and Olsen, W. C. Chlorinated Copperas - A New Coagulant. Jour. AWWA, 20 467 (1928).

13. Black, A. P. Theory of Coagulation. Water and Sewage Works, 108 R192-97 (Oct. 1961).

4. Theriault, E. J. and Clark, W. M. An Experimental Study of the Relation of $H^+$ Concentration to the Formation of Floc in Alum Solution. Pub. Health Repts., 38 181 (1923).

5. Baylis, J. R. Use of Acids With Alum in Water Purification and the Importance of $H^+$ Ion Concentration. Jour. AWWA, 10:365 (1923).

10. Miller, L. B. On the Composition of the Precipitate From Partially Alkalinized Alum Solutions. Pub. Health Repts., 38:1995 (1923).

17. Miller, L. B. A Study of the Effects of Anions Upon the Properties of Alum Floc. Pub. Health Repts., 40:951 (1925).

18. Miller, L. B. Some Properties of Iron Compounds and Their Relations to Water Clarification. Pub. Health Repts., 40:1813 (1925).

19. Barlow, E. and Patterson, R. F. Effect of Salts on the Rate of Coagulation and the Optimum Precipitation of Alum Floc. Ind. Eng. Chem., 20:831 (1928).

20. Mattson, S. J. Catapheresis and the Electrical Neutralization of Colloidal Material. J. Phys. Chem., 32:1532 (1928).

21. Black, A. P., Rice, Owen, and Barrow, Edward. Formation of Floc by Aluminum Sulfate. Ind. Eng. Chem., 25:811 (1933).

22. Barrow, Edward, Black, A. P., and Sansbury, W. E. Formation of Floc by Ferric Compounds. Ind. Eng. Chem., 25:898 (1933). Proc. ASCE, 59:1529 (1933).

23. Black, A. P. Coagulation With Iron Compounds. Jour. AWWA, 26:1713 (1934).

24. Langelier, W. F. and Ludwig, H. F. Mechanism of Flocculation in the Clarification of Turbid Waters. Jour. AWWA, 41 163 (Feb. 1949).

25. Langelier, W. F. and Ludwig, H. F. Flocculation Phenomena in Turbid Water Clarification. Proc. ASCE, 78 No. 118 (1952).

26. Milnovich, J. S., et al. Electrochemokrebic Studies of Water Coagulation. Jour. AWWA, 50:1467 (Nov. 1958).

27. Lavrenov, E., et al. Detection of Metal Ion Hydrolysis by Coagulation. III. Aluminum. J. Phys. Chem., 6:822 (1941).

28. Packham, R. F. The Coagulation Process. XIII. The Effect of pH on the Precipitation of Aluminum Hydroxide. Tech. Paper No. 17, Journ. Water Research Assn., Medmill, Surrey, England (1960).

29. Hoerle, S. Mechanism of Coagulation in Water Treatment. Jour. of San. Eng. Div. ASCE, 88 No. SA3, p. 3117-1 (May, 1962).

30. Stumm, W. and Morgan, J. J. Chemical Aspects of Coagulation. Jour. AWWA, 54:971 (Aug. 1962).

31. Black, A. P. and Christman, R. F. Characteristics of Colored Surface Waters. Jour. AWWA, 55:753 (Jun. 1963).

32. Kelley, W. P. Base Exchange of Crystalline Silicates. Ind. Eng. Chem., 37:625-30 (1945).

33. Marshall, C. E. and Krinbill, C. A. The Clays as Colloidal Electrolytes. J. Phys. Chem., 46:1077-90 (1942).

34. Helmholtz, L. F. Ann. Physik, 7:337 (1879). Has been translated. Bocquet, F. Two Memoranda on Electrokinetics. Engr. Research Bull., No. 32, University of Michigan, Ann Arbor (1951).

35. Mysels, K. J. Introduction to Colloid Chemistry, Interscience Publishers, New York (1959). p. 321.

36. Mysels, K. J. Introduction to Colloid Chemistry, Interscience Publishers, New York (1959). p. 339.

37. Black, A. P. and Willems, D. G. Electrophoretic Studies of Coagulation for Removal of Organic Color. Jour. AWWA, 53:589 (May 1961).

38. Black, A. P. and Christman, R. F. Electrophoretic Studies of Sludge Particles Produced in Lime-Soda Softening. Jour. AWWA, 53:737 (Jun. 1961).

39. Packham, R. F. The Coagulation Process - A Review of Some Recent Investigations. Progs. of the Soc. for Water Treatment and Examination, 12:15 (1963).

40. Hannah, S. A. Effects of pH and Polyelectrolyte Coagulant Aids on Coagulation of Clay Suspensions. M.S. Thesis, Dept. of Chemistry, Univ. of Florida, Gainesville, Fla. (1960). p. 24.

41. Replaceable Bases in Soils Devoid of Carbonates. Official Methods of Analysis of the Association of Official Agricultural Chemists. George Banta Publishing Co., Menasha, Wis. (8th ed., 1955). pp. 39-42.

42. Lewis, D. R. Replacement of Cations of Clay by Ion Exchange Resins. Ind. Eng. Chem., 45:1782-3 (1953).

43. Standard Methods for the Examination of Water and Wastewater. APHA, AWWA and WPCF, New York (11th ed., 1960). p. 213.

44. Cohen, J. M. Improved Jar Test Procedure. Jour. AWWA, 49:1425 (Nov. 1957).

45. Lumetron Photoelectric Colorimeter Model 450 for Nessler Tubes. Photovolt Corp., 95 Madison Ave., New York 16, N. Y.

46. Standard Methods for the Examination of Water and Wastewater. APHA, AWWA and WPCF, New York (11th ed., 1960). p. 261.

47. Standard Methods for the Examination of Water and Wastewater. APHA, AWWA and WPCF, New York (11th ed., 1960). p. 140.

48. Standard Methods for the Examination of Water and Wastewater. APHA, AWWA and WPCF, New York (11th ed., 1960). p. 114.

49. Black, A. P. and Smith, A. L. Determination of the Mobility of Colloidal Particles by Microelectrophoresis. Jour. AWWA. 54:926 (Aug. 1962).

50. Briggs, D. R. A Pyrex All-Glass Microelectrophoresis Cell. Anal. Chem., 12:703 (1940).

51. Tanbe, Norihito. Private communication.

52. Black, A. P., Singley, J. E., Whittle, G. P., and Maulding, J. S. The Stoichiometry of the Coagulation of Organic Color with Ferric Sulfate. Jour. AWWA. In press.

## BIOGRAPHICAL SKETCH

James Vernon Walters was born May 13, 1933, at Dublin, Georgia. In June, 1951, he was graduated from Dublin High School. He received the degree of Bachelor of Civil Engineering in June, 1955, from the Georgia Institute of Technology. In September of that year he enrolled in the Graduate School of the Georgia Institute of Technology. He was commissioned in the Public Health Service of the United States in November, 1956. His station of duty was the Public Health Service Regional Office in Atlanta, Georgia. That assignment continued through January, 1959. During June, 1958, he received the degree of Master of Science, Civil Engineering, from the Georgia Institute of Technology.

Mr. Walters joined the faculty of the University of Alabama as Assistant Professor of Civil Engineering in February, 1959. He continued in that position until September, 1961, when he was granted educational leave to enroll in the Graduate School of the University of Florida. From that time until the present, he has pursued his work toward the degree of Doctor of Philosophy.

James Vernon Walters is married to the former Barbara Ann Daniell. They have two sons. Mr. Walters is registered in the states of Georgia and Alabama as a Professional Engineer and Land Surveyor. He is a member of the American Chemical Society, the American Society of Civil Engineers, the American Society for Engineering Education, the American Water Works Association, the Water Pollution Control Federation, the Commissioned Officers Association of the U. S. Public Health

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Engineering and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 10, 1963

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